INVESTIGATIONS ON BIOCOMPOSITES FROM OAT HULL AND BIODEGRADABLE POLYMERS

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By

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ABSTRACT

Oat hull is an abundantly available form of biomass in Canada, which is mostly used as low-value feed material. With high fibre content, it can be used in the production of industrial products by providing opportunity as an additive in the replacement of petroleum-based products. Moreover, bio-based plastics/ biodegradable polymers are gaining popularity, as reinforced matrices into natural fibres to produce biodegradable composites. Therefore, the objectives of this investigation were to develop biocomposite materials from cellulose and lignin which were post-hydrolysis products of oat hull using biodegradable polymers (polylactic acid (PLA) and polycaprolactone (PCL)) and to compare the physical and mechanical properties of formulated biocomposites with polypropylene (PP) biocomposites so that a low-cost and eco-friendly biomaterial can be produced. Further, the effect of an impact modifier was investigated to improve the impact properties of such biocomposites.

The oat hull biomass was cleaned and chemically pretreated to produce different kinds of fibres by dilute acid hydrolysis followed by delignification at different temperature conditions. The fibres resulting from pretreatment processes were AHB (acid-catalyzed hydrolysis by-product), CRB-30 and CRB-65 (cellulose-rich biofibre). Chemical analysis of fibres showed a reduction in hemi-cellulose and lignin content, with increased cellulose content.

Formulations with rates of at 15% and 30% AHB or CRB fibres of the total mass of biocomposites were tested. The effect of impact modifier at 15% inclusion rate was also investigated with polylactic acid- and polycaprolactone-based composites. A twin screw extruder and a compression molding machine were respectively used for compounding the formulations and product molding/fabrication. The performance of the composites in all formulations was

finally assessed by measuring their physical and mechanical properties such as density, color measurement, water absorption, tensile strength, flexural strength and tensile-impact energy.

Fibre loading from 15% to 30% significantly affected the density and water absorption of the manufactured composites. The density of composites increased with addition of fibres; water absorption also increased with fibre addition in all formulations. Color analysis showed that products appeared darker in color because of addition of fibres. The results for the mechanical properties of PLA-based composites indicated that tensile and flexural strength of biocomposites generally decreased when compared to those of virgin polymers, while Young's modulus and flexural modulus increased with corresponding increase in fibre content from 15% to 30%. On the other hand, PCL-based biocomposites with 30% fibre loading offered higher flexural strength than that of composites loaded with 15% fibres; similarly, tensile modulus and flexural modulus increased with an increase in fibre content. The most significant result is that tensile-impact strength of PLA- and PCL-based composites increased with addition of an impact modifier. Therefore, eco-friendly composites were successfully developed from an oat hull biomass by-product in combination with biodegradable polymers.

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DEDICATION

I DEDICATE THIS THESIS TO MY LOVING HUSBAND AND MY PARENTS,

YOU MEAN THE WORLD TO ME

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NOMENCLATURE

AHB	Acid-catalyzed hydrolysis by-product
BS	Biomax strong 120, impact modifier
CRB	Cellulose-rich biofibres
M.C	Moisture content (%)
PCL	Polycaprolactone
PGA	Polyglycolic acid
PLA	Polylactic acid
PP	Polypropylene
RM	Raw material (oat hull)
SD	Standard deviation
w.b	Wet basis
A	Cross-sectional area (mm^2)
a_{tu}	Tensile-impact strength (kJ/m^2)
a^*	Chromacity coordinates (green to red)
b	Width of specimen in flexural test (mm)
b^*	Chromacity coordinates (blue to yellow)
d	Thickness of specimen in flexural test (mm);
E	Young's modulus (GPa)

E_f	Flexural modulus (GPa)
E_i	Impact energy (J)
ΔE	Color index
F_{max}	Maximum load in tensile test (N)
h	Thickness of sample in tensile-impact test (mm)
L	Length between support span in flexural test (mm)
L^*	Whiteness indicator (white to black)
m	Slope of the load-displacement curve
P	Maximum load in flexural test (N)
W_{dried}	Weight of sample when dry
W_{wet}	Weight of sample when wet
x	Width of sample in tensile-impact test (mm)
σ	Tensile stress (MPa)
σ_f	Flexural strength (MPa)
σ_t	Tensile strength (MPa)
ε	Extensional strain

1. INTRODUCTION AND OBJECTIVES

1.1 Background

In recent years, there has been a great awareness towards preserving our natural resources and the environment. With increased economic development and energy consumption, alternative methods and materials have been developed to replace petroleum-based products by bio-based materials. Moreover, the emphasis has been to reduce the use of petroleum-based products which are a key contributor of greenhouse gas emissions due to production of high levels of CO_2 during extraction and processing and the utilization of new renewable resources (Huda et al. 2008; Abril and Abril 2009; Kaushik et al. 2010). Bio-based materials could include industrial products made up of renewable resources such as agricultural residues. Eco-friendly biocomposites may serve as a novel alternative material in place of petroleum plastics (Mohanty et al. 2002). Biocomposites are renewable, recyclable, biodegradable and environmentally friendly resources which can be used in daily life applications in the construction, automobile, and biomedical sectors (Li et al. 2009).

Biocomposites consist of two or more phases, in which polymer matrix is reinforced with biofibres/ natural fibres (Fowler et al. 2006). The reinforcements are dispersed to the continuous matrix phase to improve mechanical properties of the composites in engineering-based applications. The properties of composites are not only dependent on the type of matrix and reinforcement, but also on the properties of phases, composition, interfacial adhesion, and geometry of the dispersed phase. However, some of the reinforcements are less effective and in

some cases, work as fillers in order to lower the material cost by cutting down the volume of the polymer matrix (U.S. Congress 1988; Fowler et al. 2007; Drathi and Ghosh 2015).

Lignocellulosic biomass is the main source for the natural fibres which can be collected from agricultural residue such as stem, leaf, and hull aside from purpose-grown fibre crops. Natural fibres can be used as fillers or reinforcements into the polymeric matrix phase for making biocomposites. The natural fibres have major advantages including low density, low cost, large-scale availability, biodegradability, non-abrasion, high stiffness, and high filling potential (Soleimani et al. 2008). Because of these advantages, natural fibre composites can be used in plastic manufacturing, furniture, packaging, including the medical, automotive, and construction industry (Li et al. 2009; Soleimani et al. 2008). There are some disadvantages that are associated with the use of natural fibres like high moisture absorption, low impact strength, and poor compatibility with the polymer matrix as well as natural fibres that cannot be processed at high temperature because of degradation of the lignocellulosic content (Soleimani et al. 2008).

Oat is one of the major grain crops in Canada and globally. Canada is a major producer of oats, according to the 36.4 million hectares of land used for agricultural production in Canada. Most of the agricultural land is located in the Canadian prairies (Alberta, Manitoba, and Saskatchewan) with 32 million hectares used for different types of crops (Sokhansanj et al. 2006). The production of oats was highest in Saskatchewan among the other provinces such as Alberta and Manitoba in the 10 year period from 1994 to 2003 (Sokhansanj et al. 2006). Oats are available in various varieties and the hull constitutes approximately 19-25% of the grain (SaskSeed Guide 2014). The factsheet of Saskatchewan Ministry of Agriculture, (November 2013), indicates that Canada produced 3.888 million tonnes/ 1.11 million hectares over the harvested area, where Saskatchewan produced almost 60% of this amount with 2.328 million tonnes/ 0.64 million

hectares harvested area (Saskatchewan Ministry of Agriculture 2013). Oat hulls are abundantly present as an agricultural by-product which can be a great source for high fibre content. Oat hull is the outermost layer of the oat grain and its pentosan content is an important raw material for the manufacture of furfural, a chemical intermediate and solvent (Quirino 2011). In terms of chemical composition, oat hull principally consists of cellulose, hemi-cellulose, and lignin, with almost equal quantities of cellulose and hemi-cellulose (ca. 30-35%), where lignin (ca. 2-10%) and ash contents (ca. 3.5-9%) are reported (Welch et al. 1983). Cellulose is semi-crystalline in nature which is contained within a layer of non-crystalline hemi-cellulose, where the components are surrounded by a matrix of hemi-cellulose and lignin. It is a polysaccharide which is made up of long chains of monosaccharide units and they are bounded by D-glucose subunits. On the other hand, hemi-cellulose is amorphous in nature, partly soluble in water, and has low strength. It is a matrix of polysaccharides with different sugar monomers which is formed by branches with short lateral chains. Lignin is an amorphous heteropolymer which is insoluble in water. Lignin has a three-dimensional structure with phenylpropane monomeric units (Anderson 2007; Ruffell 2008; Marais 2009).

Oat hull biomass has been investigated for the production of xylitol by integrated processes of acid-catalyzed hydrolysis and bioconversion (Soleimani and Tabil 2012). Oat hull was cleaned, dried, and pretreated first using hydrolysis. Dilute acid hydrolysis was performed for the depolymerisation of hemi-cellulose and to recover the maximum amount of sugars (Chandel et al. 2012; Soleimani 2013).The hemi-cellulose portion from the hydrolysis was used for the conversion of xylose to xylitol and the process parameters were optimized to maximize the production of xylitol (Soleimani 2013). The by-product from the hydrolysis, other species besides hemi-cellulose include components rich in cellulose and lignin, which represent a great source of fibre to be used

as filler/reinforcement for the production of biocomposites. The cellulose fibres have been reinforced into the polymer matrix and the biocomposites derived from polypropylene and fibres have approximately same strength as that of virgin polypropylene (Soleimani and Tabil 2012).

There are also some limitations associated with natural fibres such as high water absorption characteristics as fibres are highly polar materials. On the other hand, there are polymer matrices which are hydrophobic and non-polar in nature as compared to natural fibres. As a result, the difference in the properties of components of biocomposites led to weak interfacial bonding between polymer matrix and fibre which in turn influence the mechanical properties of the finished products (Li et al. 2007; Zafeiropoulos 2008). Therefore, a number of investigations have been carried out to improve adhesion between natural fibres and polymer matrix. Surface modification was done successfully by treating natural fibres with physical and chemical methods such as corona treatment, plasma treatment, mercerisation, and heat treatment and silane coupling method, esterification, and graft copolymerisation, respectively (Wang et al. 2008; Zafeiropoulos 2008).

Natural fibre-reinforced biocomposites using biodegradable polymers have been claimed as the most environmentally friendly bioproducts (dos Santos Rosa and Lenz 2013). A few studies have been conducted on the manufacture of biocomposites with the use of biodegradable polymers and oat hull fibres. Therefore, biocomposites are possible using biodegradable polymers such as polylactic acid (PLA) and polycaprolactone (PCL), depending on their desired properties and the end-use of the product, their biocompatibility with the fibre, synthesis, and biodegradation rate of the polymer (Gunatillake and Adhikari 2003). Moreover, the performance of biocomposite depends on such factors as fibre volume or weight fraction, nature of the matrix, and fibre-polymer matrix compatibility. Therefore, by applying different physical and chemical treatments,

renewable and biodegradable composites could be developed from different kind of fibres and polymers.

1.2 Objectives

The main objective of this project is to develop biocomposite materials from cellulose and lignin derived from acid hydrolysis combined with partial delignification of oat hull. Biocomposites using PLA and PCL were formulated by reinforcement or filling with oat hull biofibres and then compared the physical and mechanical properties of these biocomposites with polypropylene (PP) biocomposites to afford low-cost and eco-friendly biomaterials. The specific objectives are:

1) to investigate the effect of fibre inclusion rate of acid-catalyzed hydrolysis by-product (AHB) derived from oat hull prior to delignification by comparing the physical and mechanical properties of PLA- and PCL-biocomposites with that of PP-biocomposite materials;
2) to determine the effect of different inclusion rates of delignified fibres called as CRB (cellulose-rich biofibres) by comparing the physical and mechanical properties of PLA- and PCL-biocomposites with PP-biocomposites; and
3) to study the effect of an impact modifier on the physical and mechanical properties of PLA- and PCL-biocomposites made of CRB.

The different fibre inclusion rates for the PLA- and PCL-biocomposites were chosen by studying and reviewing available literature. Previous work has been done to study the effect of flax fibre loading, with use of compatibilizer and pretreatment on the properties of flax fibre-polypropylene composites with observed improvements in various physical and mechanical properties (Soleimani et al. 2008).

1.3 Organization of the Thesis

The entire thesis is divided into six chapters. Chapter 1 represents an introduction to the composites with background on oat hulls and which is followed by objectives of the project. The literature survey related to this study is described in Chapter 2. It includes study on lignocellulosic biomass and different pretreatment methods for the production of natural fibres. It also covers the study of biocomposite materials obtained from natural fibres and polymer matrix. To attain the objectives, a systematic study was carried out and the details of experimental procedures, materials, equipment, test methods, and their physical and mechanical characterization techniques are discussed in Chapter 3. Chapter 4 provides the results of experimental data for manufactured biocomposite materials. The results of physical (chemical analysis, color, density, and water absorption) and mechanical tests (tensile properties, flexural properties, and tensile-impact properties) are presented and discussed. Chapter 5 summarizes this research study and provides conclusions based on the results from Chapter 4. Some recommendations for future work are included in the last chapter.

2. LITERATURE REVIEW

Various research methods have been developed for the production of composites from agricultural residues and polymer matrices. However, very limited work has been done on oat hull-reinforced or oat-hull filled biocomposites thus far. At the time of the writing of this thesis, no reported work was found related to oat hull and PCL-based biocomposites. Therefore, to achieve the introductory objectives, the literature was reviewed for the development and modifications of biocomposites with desirable properties.

2.1 Oat grain composition, processing and extraction methods

Oat is an important cereal grain worldwide. It is mainly used as animal feed, alone or in mixture. It is used as food in the form of breakfast cereals (Suttie and Reynolds 2004). Oat grain have an outer covering called oat hull. The oat hull cell wall is comprised of major components such as cellulose, hemi-cellulose, and lignin along with ash. Different varieties of oats contained approximately up to 25% of the oat hull (SaskSeed Guide 2014). The cellulose and hemi-cellulose (ca. 30-35%) are of equal compositions, lignin (ca. 2-9%), and ash content (ca. 3.5-9%). The protein and oil content in oat hulls are low, 1.6-5% and 1-2.2%, respectively; whereas, the kernel has up to 40-60% of protein with 5-30% oil content (Welch et al. 1983).

Oat milling is the process to separate the oat groats from hulls by undergoing different processing stages such as cleaning, drying, and dehulling. The raw oats are cleaned using screens before processing. Oats are to be roasted or steamed first to facilitate separation and then a rotating drum is used to mechanically separate oat hulls from the kernel part prior to milling. By air aspiration hulls and groats are removed (Suttie and Reynolds 2004).

2.1.1 Lignocellulosic biomass: structure and composition

The raw material for lignocellulosic biomass comes in various forms which can be classified as woody- and non-woody biomass, dedicated energy crops, organic waste etc. The woody biomass such as forest residues include the material left in natural forest, forestry waste, branches from dead trees, etc. In the forestry industry, waste generated from logging operations of trees, mill processing operations such as saw dust from saw mills and wood chips. The salvage is also collected from the damage by wildfire and due to insect and disease infestation in the forest. Dedicated energy crops are plants which can be grown for the production of bioproducts other than food or feed. These contain woody and non-woody biomass resources which can be planted and harvested in a short period of time. Dedicated energy crops contain energy-rich components such as oils, sugars, starches, and lignocellulose. These can be classified into herbaceous energy crops and short-rotation woody crops. Organic waste materials such as animal waste, sludge, yard waste, food processing waste, and municipal solid waste are biomass resources that can be used for energy production. The municipal solid waste is household garbage, which is the largest volume of waste worldwide and solid disposal methods are very costly. Therefore, use of solid waste as a biomass resource can be very effective (Brown 2003).

The non-woody biomass includes agricultural residues such as field residues and processing residues. Field residue is the leftover material in the agricultural field after harvesting the crops and it includes straw, leaves, stalks, and seed pods. Processing residue is the material remaining after the processed crop is converted into a usable resource such as bagasse, hulls, seeds, and roots. The major agricultural residues are wheat straw, oat straw, oat hulls, rice husk, rice straw, corn stover, rye straw, canola straw, sugarcane bagasse, and many others which are readily available and of very low cost. The alternative use of these residues is that aside from biomass, the

residues are specially used for soil conditioning and to increase the levels of soil organic matter, to prevent soil erosion, to increase the water holding capacity of soil, and to increase the overall soil fertility (Brown 2003).

Lignocellulose is the main part of the plant cell wall which imparts strength and structural support to the plant and is composed of cellulose, hemi-cellulose, and lignin and also contains small levels of proteins, pectins, extractives (such as waxes, soluble nonstructured sugars, nitrogenous materials, etc.), and ash. However, biomass is comprised of different species and lignocellulosic content is different for each plant species. The percentage of composition along with different species also changes with the age, growth, and other conditions of the plant (Xu et al. 2007).

Lignocellulose has a complex structure as shown in Figure 2.1, where cellulose microfibrils are wrapped in between hemi-cellulose and lignin, which acts as a protective layer; therefore it is very challenging to breakdown this complex structure.

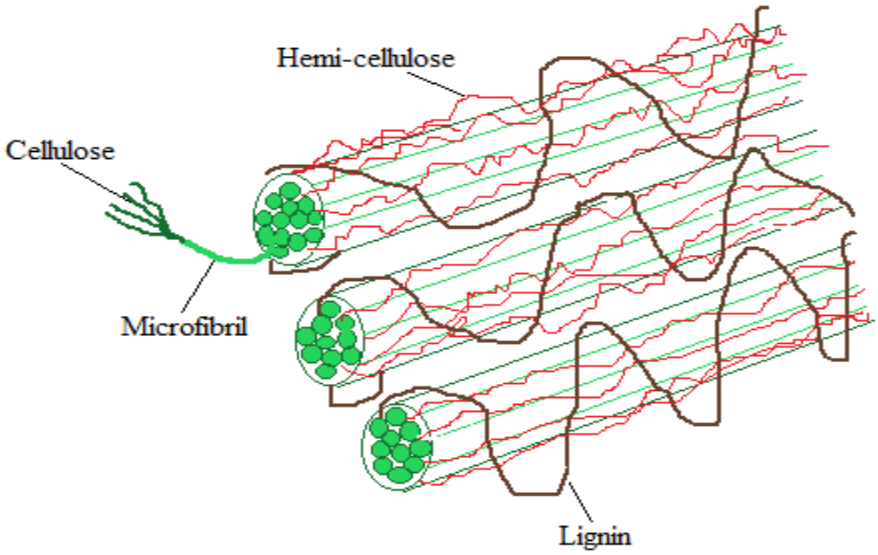


Figure 2.1. Structure of lignocellulosic biomass in the plant cell wall.

Cellulose is the major portion of lignocellulosic biomass. It is fibrous in nature, tough and water-insoluble substance and can be found in the stems, stalks, and in other portions of the plant and other agricultural materials (Tabil et al. 2011). Therefore, these properties contribute to the mechanical strength and chemical stability to the plant cell walls. Cellulose is present in the form of crystalline and amorphous regions in the lignocellulosic biomass which can be isolated from the plants (Anderson 2007; Grewal et al. 2012). The crystalline portion has the higher percentage, while amorphous region is present in small fractions as unorganized cellulose chains. It is easier to breakdown the amorphous structure of cellulose as the molecules are loosely packed. Cellulose is a polysaccharide, consisting of carbon, hydrogen, and oxygen $(C_6H_{10}O_5)_n$ and the chemical structure of cellulose is shown in Figure 2.2. It is made up of repeating units called as cellobiose which is formed by two glucose monomers. The cellobiose forms the long chains and the cellulose microfibrils are formed due to hydrogen and van der Waals bonds which form tightly packed crystallites (Anderson 2007; Ruffel 2008).

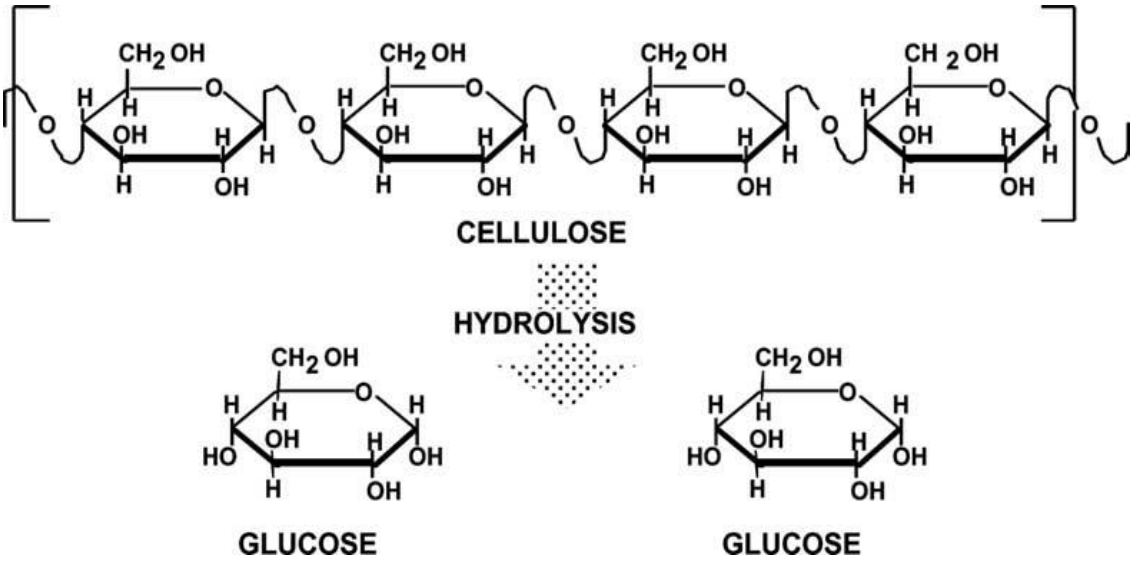


Figure 2.2. Structure of cellulose and its hydrolysis (adapted from Iroba 2014).

Hemi-cellulose is the second most common polysaccharide found in the lignocellulosic material. Hemi-cellulose is present in all plant cells along with cellulose. Hemi-cellulose is soluble in water at high temperatures but it is insoluble in water at low temperature. Its molecular weight is lower than that of cellulose and it connects the cellulose microfibrils and lignin together. Hemi-cellulose is amorphous in nature and possesses low strength, but it provides structural integrity to the plant because of branched structural forms. It is a branched heterogeneous polymer which is made up of short-chained polysaccharides with different sugar units. These heteropolymers are mainly composed of pentose (xylose, rhamnose, and arabinose), hexose (glucose, mannose, and galactose), and uronic acids (4-O-methyl-glucuronic, D-glucuronic, and D-galacturonic acids). Hemi-cellulose biopolymers contain acetyl and methyl groups, where the most common form is xylan. Hemi-cellulose is branched according to substitution at different carbon sites; β-(1,4)-glycosidic bonds and occasionally by β-(1,3)-glycosidic bonds. In hemi-cellulose, xylose is present in large quantities with xylan as a backbone attached to other groups. Hemi-cellulose and cellulose are bonded to each other by hydrogen bonds with lignin attached to hemi-cellulose in a covalent manner. Therefore, hemi-cellulose is incorporated between cellulose and lignin, but it can be easily hydrolysed by strong acid and/ or a strong base, leaving cellulose and lignin undissolved (Anderson 2007; Ruffel 2008; Khanok 2013; Iroba 2014).

Lignin is a complex natural polymer and is the most abundant in nature. Lignin is present in the cell walls along with cellulose and hemi-cellulose. It gives structural support to the plant according to its high mechanical strength, impermeability and lignin is extremely resistant towards chemical and biological degradation (Ruffell 2008). It acts as a binder for the cells and cements the cellulose and hemi-cellulose together with itself, where the content of lignin varies among different plants. The percentage of carbon in lignin is much higher than in cellulose. It also contains

small amount of proteins, pectins, extractives, and ash. The combination of lignin and crystalline cellulose, with covalent and hydrogen bonding preserves the plant cellulose from the attack of microorganisms (Kinsley 2014). In this three-dimensional structure of amorphous heteropolymer, phenyl-propane has three common monomer units; *coniferyl alcohol (guaiacyl propanol), p-coumaryl alcohol (p-hydroxyphenyl propanol), and sinapyl alcohol (syringyl alcohol)* which are linked together through different C-O bonds and C-C bonds (alkyl-aryl, alkyl-alkyl, and aryl-aryl) (Ruffell 2008; Khanok 2013; Iroba 2014).

Apart from cellulose, hemi-cellulose, and lignin, there are also presence of additional compounds in the lignocellulose called extractives and non-extractives. These extraneous materials are present in small quantities and are of very small molecular size. These can be separated from the lignocellulosic structure without deteriorating it through polar and non-polar solvents. The different categories of these materials include waxes, fats, alcohols, resins, and many other cytoplasmic components such as extractives and inorganic compounds as non-extractives. Also, the variety of extraneous material is different in each biomass which depends on the type of biomass.

2.1.2 Pre-processing and pretreatment of biomass

Before the pretreatment of lignocellulosic biomass several pre-processing operations have to be undertaken like drying, densification, collection and handling of biomass, storage, and transportation to the plant. For example, the biomass agricultural residue can be dried in the fields to lower down moisture content. After drying, the biomass is collected from the fields and sent to the storage (Brown 2003).

Pretreatment is the first step for the conversion of biomass into various bioproducts. It is done to break down the structure of lignocellulose by separating cellulose, hemi-cellulose, and lignin. Figure 2.3 shows the breakage of lignocellulosic structure of biomass by a pretreatment method.

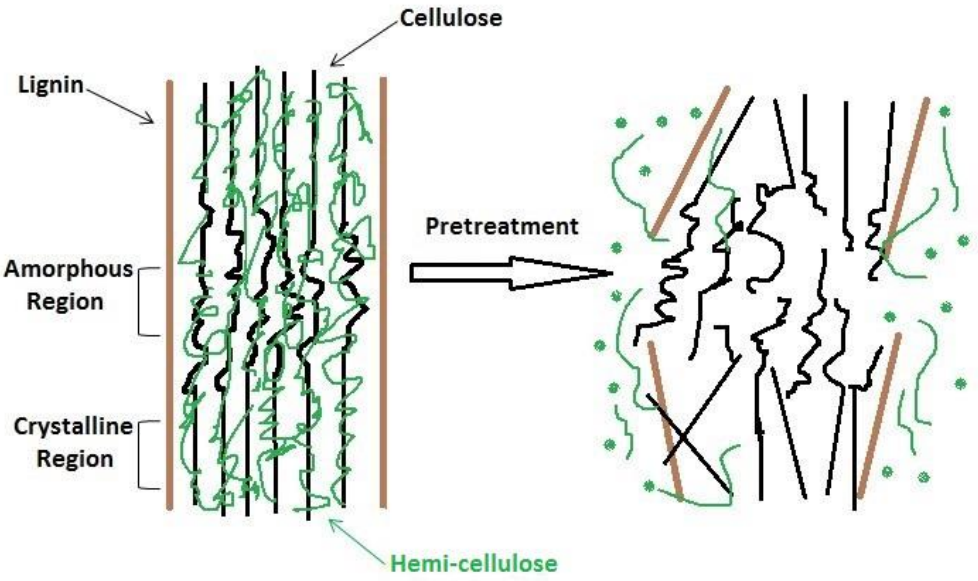


Figure 2.3. Breakage of lignocellulosic structure by pretreatment (adapted from Brodeur et al. 2011).

The main purpose of pretreatment is the removal of lignin and hemi-cellulose from the lignocellulosic biomass with reduced crystallinity in cellulose and increase in the porosity (Sun and Cheng 2002). The pretreatment process must fulfill the following functions in order to ease the hydrolysis process: (1) increase in the porosity and the surface area; (2) breakage of the lignin compound; (3) hemi-cellulose removal; (4) lignin removal; (5) reduce the crystallinity of the cellulose; (6) preservation of the carbohydrates; (7) prevent formation of inhibitory by-products; (8) be cost effective and minimize the energy demand; (9) lower the generation of residues; and

(10) more rapid and higher yield by hydrolysis (Sun and Cheng 2002; Harmsen et al. 2010; Iroba 2014).

The pretreatment processes have been reviewed by many articles in detail and are classified into different categories of physical, chemical, physicochemical, and biological pretreatment methods, which are briefly introduced (Sun and Cheng 2002; Galbe and Zacchi 2007; Taherzadeh and Karimi 2008; Brodeur et al. 2011; Verardi et al. 2012; Iroba 2014).

2.1.2.1 Physical methods

The physical pretreatment methods are done mechanically or non-mechanically for particle size reduction. Mechanical pretreatment includes milling, grinding, chipping etc. and these processes result in conversion of the material into a fine powder form (Galbe and Zacchi 2007; Iroba 2014). By reduction in the particle size, it is easier to handle and store the biomass (Harmsen et al. 2010). Also, if the material has to be transported, it is very convenient to reduce the size as the cost of transportation decreases by compaction of the material. The cost for all operations is also very necessary as large amount of energy is to be used for the size reduction. The energy for the physical methods depends on the size of the particle and its crystallinity. By physical pretreatment, the crystalline structure of the cellulose is reduced which will ease the hydrolysis process for lignocellulosic biomass. On the other hand, size reduction increases the surface area of the particles which will improve the mass transfer characteristics (Brodeur et al. 2011).

Another physical pretreatment method is irradiation which is also used to lower the crystallinity of the cellulose and to increase the surface area. In this method, gamma rays are used to dissect the β-(1,4)-glycosidic bonds. However, this method is very expensive to be used on a large scale (Galbe and Zacchi 2007).

2.1.2.2 Chemical methods

In this method, pretreatment is completely done by chemicals and the biomass structure is disrupted by chemical reactions (Harmsen et al. 2010). Chemical pretreatment is considered as the most effective method with minimum formation of inhibitors. Apart from the advantages of these methods, there is a requirement of specialized corrosion-resistant equipment, extensive washing of the product, and proper disposal of the chemical wastes (Anderson 2007; Iroba 2014). Various types of chemical pretreatment such as acidic hydrolysis, alkaline hydrolysis, and organosolv process are briefly described below (Sun and Cheng 2002; Galbe and Zacchi 2007).

Acidic hydrolysis can either be concentrated acid or dilute acid hydrolysis. In each process, biomass is soaked in the acidic solution and heated to the desired temperature for a certain period of time (from min to h), where the hemi-cellulose is hydrolysed to remove the cellulose fraction as the main component in the form of monomer sugars (Galbe and Zacchi 2007).

In the case of alkaline hydrolysis, the material is soaked in an alkaline solution and heated for some time. It helps in swelling of the pores of the cellulosic chains with an increase in the surface area and a decrease in the crystallinity of cellulose. Alkaline pretreatment breaks the bonds between lignin and carbohydrates, and disrupts the lignin structure (Sun and Cheng 2002; Galbe and Zacchi 2007).

Another method is the organosolv process which breaks the bonds between lignin and hemi-cellulose by using an organic or aqueous-organic solvent mixture in addition with an inorganic acid catalyst. In this method the lignin is hydrolysed and recovered as an organophilic phase. The solvents used are mainly ethanol, methanol, acetone, ethylene glycol, tri-ethylene glycol, and phenol. And sometimes, these solvents are difficult to handle as some of them are highly flammable and explosive (Galbe and Zacchi 2007).

2.1.2.3 Physicochemical methods

These methods are combination of both physical and chemical methods as these involve mechanical and chemical techniques to alter the structure of biomass. Some of the methods used in this category are steam explosion, AFEX (ammonia fibre explosion), and CO_2 explosion (Sun and Cheng 2002; Harmsen et al. 2010).

Steam explosion is the most commonly used method in the pretreatment of biomass because of the low use of the chemicals and low energy consumption. In this method, the biomass is reacted with high pressure steam which is injected into the batch or continuous reactor. The temperature is increased during the steam injection in between 160° - 260°C. The material is held for a certain period of time and after some time, the pressure inside the reactor is reduced suddenly which results in the hemi-cellulose degradation and disruption of the lignin structure with an explosive decompression (Sun and Cheng 2002; Harmsen et al. 2010). This method produces material in a slurry form which again can be separated into solid and liquid fractions (Taherzadeh and Karimi 2008).

Ammonia fibre explosion (AFEX) is the alkaline physicochemical method which uses liquid ammonia for the pretreatment of the biomass. This method is similar to steam explosion but it operates at lower temperature than the steam explosion method. The typical conditions for the biomass to be treated with liquid ammonia are at high pressure for 30 min residence time and 90° - 100°C temperature, using 1-2 kg ammonia/kg of dry mass. With this process, the lignin content is reduced but the hemi-cellulose and cellulose remain intact (Taherzadeh and Karimi 2008; Harmsen et al. 2010).

Carbon-dioxide explosion method is another improved pretreatment technique which uses high pressure CO_2 in the batch reactor. It was observed that carbonic acid is formed by reacting CO_2 with water; by that, the hydrolysis rate of hemi-cellulose and cellulose can be increased. However, the yields are lower than ammonia fibre explosion and steam explosion (Taherzadeh and Karimi 2008; Harmsen et al. 2010).

2.1.2.4 Biological methods

In this method, micro-organisms are used for the degradation of the lignin and hemi-cellulose in the biomass. Thus it is considered as the safest and most environment friendly pretreatment as no chemicals are required (Galbe and Zacchi 2007; Verardi et al. 2012). It uses very low energy with mild operating conditions (Harmsen et al. 2010). Micro-organisms such as fungi (white-, brown-, and soft- rot fungi) are mainly employed for the degradation of lignin and hemi-cellulose in biomass (Sun and Cheng 2002). The degradation of the lignocellulose is activated by these micro-organisms at mild conditions. Lignin and cellulose are both degraded by white- and soft- rot fungi, while the brown- rot fungi mostly attacks cellulose (Ruffel 2006). This method is not so popular on the industrial scale, because it is very slow and also some of the main constituents of the lignocellulose compounds are also degraded by micro-organisms; however it can be used to initiate the process (Galbe and Zacchi 2007).

All the above methods are used for the pretreatment of lignocellulosic biomass and all have some advantages and disadvantages. Furthermore, different methods yields different results and one could choose a method that will serve their research purpose.

2.1.3 Fibre extraction methods

Natural fibres are extracted from lignocellulose by hydrolysis using acids or bases with a combination of heat (Abril and Abril 2009).Acid hydrolysis is considered as the most effective and widely used industrial method for the degradation of lignocellulosic structure of biomass (Abril and Abril 2009). It is a simple method which hydrolyzes lignocellulosic biomass at a rapid rate (Parisi 1989). The acids used for the hydrolysis of biomass include sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3) (Canilha et al. 2012; Iroba 2014). This chemical process can be achieved either by concentrated acid hydrolysis or by dilute acid hydrolysis.

2.1.3.1 Concentrated acid hydrolysis

Concentrated acid hydrolysis is known to give higher yields at lower temperature (e.g. 40°C) in comparison to dilute acid hydrolysis. But concentrated acid is toxic, corrosive, and hazardous in nature, and a large amount of acid (ca. 30 – 70%) is required for the process. Therefore, the reactors must also be corrosion resistant and could be made of specialized non-metallic construction material (Taherzadeh and Karimi 2007; Zheng et al. 2009). Furthermore, after the production of hydrolysate, the concentrated acid must be recovered and reused in order to make the process economically feasible (Zheng et al. 2009). Thus, significant increase in the overall cost has reduced the utility of this process (Taherzadeh and Karimi 2007; Iroba 2014).

2.1.3.2 Dilute acid hydrolysis

On the other hand, dilute acid pretreatment is the most preferable method among acid hydrolysis methods and has been utilized commercially for the hydrolysis of various lignocellulosic biomass (Zheng et al. 2006; Zheng et al. 2009; Brodeur et al. 2011). The greatest benefit of dilute acid hydrolysis over concentrated is the low acid consumption with fast reaction rates (Alriksson 2006).

The most commonly used acid is sulfuric acid. A review of the literature indicates that sulfuric acid with less than 4% (w/w) is the most effective and inexpensive way to pretreat the lignocellulosic biomass (Kumar at al. 2009; Kinsley 2014). Dilute sulfuric acid has been commonly used for the production of furfural from lignocellulosic biomass by hydrolyzing hemi-cellulose to xylose and finally to furfural (Kumar at al. 2009; Brodeur et al. 2011). Waste cotton (products) have also been subjected to acid hydrolysis for the preparation of cellulose nanocrystallites and the behaviour of different cellulosic fibres have been studied by a levelling off in the degree of polymerization (LODP) (Kaushik and Kaur 2011; Hai et al. 2015; Palme et al. 2015). For dilute acid hydrolysis of lignocellulosic biomass, different types of reactors have been used such as batch, plug flow, percolation, counter-current, and shrinking-bed reactors (Purwadi 2006; Taherzadeh and Karimi 2008). Dilute acid pretreatment is also effective in the separation process of lignocellulose biomass by removing almost 100% of hemi-cellulose from cellulose and lignin. However, lignin removal is not possible but there is disruption in the structure of lignin. Furthermore, pure cellulose has been extracted from lignin by undergoing alkaline pretreatment (Taherzadeh and Karimi 2008; Brodeur et al. 2011).

Generally, there are two types of dilute acid hydrolysis (Harmsen et al. 2010):

a. At high temperature, continuous flow with low solid loadings (T >160°C, weight of the substrate = 5-10%)
b. At low temperature, batch flow with high solid loadings (T <160°C, weight of the subtrate = 10-40%)

During dilute acid hydrolysis, various process parameters such as temperature, time, acid concentration, and solid-to-liquid ratio play an important role in the kinetics of agricultural residues and the yield of the end-product also depends on these parameters (Chandel et al. 2012).

Also, different types of biomass have variable lignocellulosic composition which affect the final yield of sugars by the hydrolysis process. Additionally, some disadvantages are also associated with dilute acid hydrolysis such as low sugar yields, high temperature requirements, hemi-cellulose sugar degradation, and formation of inhibitory substances (Saha et al. 2005; Alriksson 2006). However, these difficulties could be minimized by applying different techniques. For example, inhibitor formation has been reduced by applying detoxification steps (Purwadi et al. 2004; Abril and Abril 2009).

The batch process is the simplest method for the dilute acid hydrolysis and is the most widely used on laboratory and pilot scale for the kinetic study of hydrolysis (Taherzadeh and Karimi 2007). Batch hydrolysis with dilute acid pretreatment can be performed in one stage or two stages (Taherzadeh and Karimi 2007; Chandel et al. 2012).

A study conducted by Taherzadeh et al. in 1997 reported that using a one-stage hydrolysis process, where 0.5% sulphuric acid was treated with the biomass at 188 - 234°C for 7 min of retention time, where more than 80% hemi-cellulose was recovered. Taherzadeh and Karimi (2007) published a review article entitled "acid-based hydrolysis processes for ethanol production". They reported drawbacks associated with one-stage dilute-acid hydrolysis, which involved sugar degradation in the hydrolysis reactions in combination with several undesirable by-products. In addition, they stated that it lowered the yield of sugars and slowed down the ethanol formation in the fermentation process due to the by-products.

Therefore, in order to reduce the degradation of sugars at higher temperature and for maximizing the yield with less formation of inhibitors, two-stage hydrolysis is preferred (Alriksson 2006; Taherzadeh and Karimi 2007). In first stage of this method, biomass is treated with dilute

acid at mild temperature conditions of approximately 170 - 190°C and hemi-cellulose is hydrolysed to sugar monomers with yield of more than 80%; while in the second stage, cellulose is converted into glucose at a much higher temperature of approximately 200 - 230°C, offering an overall maximum yield (Galbe and Zacchi 2002; Alriksson 2006; Taherzadeh and Karimi 2007). Moreover, a two-stage dilute-acid hydrolysis is often adopted because of the minimum energy requirements over one-stage dilute-acid hydrolysis (Taherzadeh and Karimi 2007; Chandel et al. 2012).

2.1.4 Detoxification methods

The inhibitors produced in the dilute acid hydrolysis such as acetic acid, formic acid, furfural, and phenolic compounds are toxic to microorganisms, which can negatively affect the efficiency of further fermentation processes (Taherzadeh and Karimi 2007; Hsu et al. 2010; Brodeur et al. 2011; Babu et al.2013; Jonsson et al. 2013). Several detoxification methods were developed such as physical, physicochemical, and biological processing to minimize the concentration of toxic compounds in the hydrolysate (Carter et al. 2011; Canilha et al. 2012; Babu et al.2013; Jonsson et al. 2013).

The physical methods of detoxification are evaporation and use of membrane filtration. In the evaporation method, the volatile substances such as acetic acid, furfural, formaldehyde are vaporized from the hydrolysate by vapour and vacuum evaporation with increased sugar concentration. However, this method has a disadvantage of increasing non-volatile toxic compounds such as extractives and derivatives of lignin (Canilha et al. 2012; Babu et al.2013). While membrane filtration has offered several advantages by eliminating metabolic inhibitors, the

surface functional groups of toxic compounds represent challenges due to attachment within the internal pores of the membrane (Canilha et al. 2012).

On the other hand, physicochemical methods remove toxic compounds by using different detoxification treatments such as ion exchange resins, activated charcoal, overliming, neutralization, and extraction by organic solvents. In the ion exchange resin process, most of the acetic acid, furfural, and lignin derived inhibitors are ionized without any damage to the resin. While phenolic compounds are mainly removed by adsorption process of activated charcoal with the advantage of relatively low cost. The most common and widely used detoxification method is the alkali treatment in which addition of lime or neutralization compounds such as sodium or potassium hydroxide have been used to precipitate the toxic compounds. This method eliminates most of the acetic acid, furfural, soluble lignin, and phenolic compounds from the hydrolysate and increase its fermentability index. Some of the organic solvents such as ethyl acetate, trichloroethylene, and chloroform have also been used in the extraction of inhibitors in the detoxification process (Carter et al. 2011; Canilha et al. 2012; Babu et al.2013).

Biological methods require the use of certain enzymes and microorganisms for the detoxification treatment of inhibitory compounds. As compared to physical and chemical methods, this detoxification process may be carried out directly in the same fermentation vessel. In addition, this method requires very low energy and very low waste is produced. Therefore, it has been considered as the most environment friendly method, with one disadvantage of long processing times (Canilha et al. 2012).

2.1.5 Oat hulls hydrolysis

In Canada, Iogen Corporation of Ottawa, ON in collaboration with University of Toronto in 2001, have used oat hull hydrolysate in combination with different *Zymomonas mobilis* recombinants to

comparatively study the productivity of ethanol. They opted for Iogen process of dilute sulfuric acid with combination of steam explosion for the depolymerisation of biomass by disrupting hemi-cellulose and cellulose for the preparation of hydrolysate for ethanol production (Lawford et al. 2001). Soleimani and Tabil (2012) also investigated xylitol production from oat hulls by dilute-acid hydrolysis. Oat hulls were subjected to dilute sulfuric acid hydrolysis under two different reaction conditions, i.e. atmospheric and pressurized reactor. Both experiments were performed with variable process parameters of acid concentration, temperature, and residence time. Kinetics of hydrolysis yield under different reaction conditions was studied through each process parameter. Other than xylitol, the by-product of hydrolysis was rich in cellulose and lignin which have been extracted in the solid form, i.e. fibres. These extracted fibres have been used in the production of biocomposites (Soleimani and Tabil 2102; Soleimani 2013).

2.1.6 Delignification of fibres

Delignification of lignocellulosic biomass can further be performed after dilute acid hydrolysis in order to recover most of the cellulosic fibres by solubilizing lignin. Lignin could be further used in industrial processes by converting into a fuel (Abril and Abril 2009). Delignification can be achieved by alkaline hydrolysis with the use of various bases such as sodium hydroxide, calcium hydroxide, aqueous ammonia, ammonium hydroxide etc. (Zheng at al. 2009). It can be done under mild temperatures but needs longer residence time up to hours or days with higher concentration of alkali (Iroba 2014). Alkaline treatment by sodium hydroxide has been reviewed (Kumar at al. 2009). After soaking of lignocellulosic materials in the alkaline medium with some heating, it results in swelling of the pores. In turn, an increase of the internal surface area occurs with a decrease in degree of polymerisation and crystallinity, degradation of lignin structure, and breakage of bonds between lignin and carbohydrates (Sun and Cheng 2002; Galbe and Zacchi

2007; Zheng at al. 2009; Harmsen et al. 2010). Thereafter, natural fibres were reported to be free from hemi-cellulose, lignin, waxy substances, natural oils, and any other impurities (Mohanty et al. 2001; Rodriguez and Vazquez 2006; Rokbi et al. 2011; Kim et al. 2012). Studies have also revealed that alkaline-treated natural fibres have a rough surface topography which assist the process of interlocking between fibre and polymer matrix by allowing additional pore sites (Agarwal et al. 2000; Rodriguez and Vazquez 2006; Wang et al. 2008; Zafeiropoulos 2008; Rokbi et al. 2011). Moreover, there is also increase in the number of hydroxyl groups on the surface of fibre which lead to proper adhesion of fibres with resins such as polyester or vinylester (Rodriguez and Vazquez 2006). Also, alkali treated natural fibres are recognized to have improved interfacial bond strength between fibre and matrix by increasing mechanical properties of composites such as stiffness and flexural moduli (Ramadevi et al. 2012). A study by Kim and co-workers (2012) on the empty palm fruit bunch fibres investigated the sequential pretreatment of fibres with dilute acid hydrolysis followed by alkali treatment. Dilute sulfuric acid treatment was effective in reducing hemi-cellulose and lignin content in empty fruit palm bunch fibre by 90% and 32%, respectively; which was followed by delignification with sodium hydroxide. The final yield of cellulose, hemi-cellulose, and lignin were reported to be 82%, 1%, and 30%, respectively, in the case of empty palm fruit bunch fibres (Kim et al. 2012). The composition of oat hull fibres after dilute acid hydrolysis and alkali treatment were reported by Soleimani and Tabil (2012). Therein, the hemi-cellulose and lignin content was reduced to 0% and 7%, respectively, with rest of the cellulose in the form of extracted fibres. Alkaline treatment to jute fibres was employed with 5% NaOH solution at 30^{o}C with varied immersion time of 2, 4, 6, and 8 h. The resulting composites with 4 h of immersed fibres have shown improved mechanical properties (Ray et al. 2001). By comparison, a study of composites with alfa fibres has shown increased flexural strength and

modulus with fibres soaked in 10% NaOH for 24 h and suggested for use as a reinforcement material (Rokbi et al. 2011).

2.2 Biodegradable polymers

Polymer degradation may occur in different environments by exposure to sunlight, through oxidation or hydrolysis by water and by the action of microorganisms. In addition, the degradation of high molecular weight plastics proceeds first by photochemical or chemical reactions to reduce the molecular weight and then followed by microbial attack. The structure of polymers was disassembled first by hydrolysis, which separates it into monomers and then these macromolecules were broken down into small molecules by enzymatic/microbial attack. These mechanisms results in the release of toxic compounds which are very harmful to the surroundings, mostly in the case of traditional petroleum-based plastics (Lampman 2003; Duhovic et al. 2008; Tokiwa et al. 2009; Vroman and Tighzert 2009; Lambert 2013). Therefore, these environmental risks can be reduced by the use of biodegradable polymers because upon their biodegradation under a controlled environment, no hazardous chemicals are released into the environment. Moreover, biodegradation for biopolymers and their composites may occur in the four main environmental compartments through soil, water, landfilling, and composting (Duhovic et al. 2008). Additionally, biodegradable polymers should have advantages over synthetic and non-biodegradable plastics for sustainable and reliable product life, including renewability, recyclability, and comparable properties to that of non-biodegradable polymers (Duhovic et al. 2008; Staiger and Tucker 2008).

Biodegradable polymers are derived from either renewable or non-renewable resources (Duhovic et al. 2008; Tokiwa et al. 2009; Salit 2014). Many of the biodegradable polymers studied belong to the aliphatic polyester family such as polylactic acid (PLA) and polycaprolactone (PCL) and have been widely used in the replacement of non-biodegradable plastics (Gunatillake and

Adhikari 2003; Tokiwa et al. 2009; dos Santos Rosa and Lenz 2013). Furthermore, biodegradability of these polyesters is dependent on various chemical and physical properties such as chemical structure, molecular weight, crystallinity, melting temperature, glass transition temperature, and surface conditions. The degree of crystallinity is the major factor affecting biodegradability of polymers, as the amorphous regions are more susceptible to enzymatic attack than crystalline part in which molecules are closely packed (Tokiwa and Calabia 2007; Tokiwa et al. 2009).

PLA is thermoplastic in nature and can be derived from numerous renewable resources such as corn starch, sugarcane, sugar beet, or tapioca (Islam 2008; Talimi 2011; Hassan et al. 2013; Salit 2014). It is polymerised from lactic acid by the process of either polycondensation or ring-opening polymerisation which can be found in the form of two optical isomers: L- and D- lactide (Figure 2.4) (Qu et al. 2010; Averous and Pollet 2012; dos Santos Rosa and Lenz 2013; Salit 2014). PLA has high biocompatibility, hydrophobic, low degradation rate, improved thermal processability, and good mechanical properties compared with other biodegradable polymers. However, the major drawback with the use of PLA is its brittleness (low flexibility) (Gunatillake and Adhikari 2003; dos Santos Rosa and Lenz 2013). In order to overcome brittleness, certain additives or impact modifiers have been developed to improve impact properties of composites. Several studies have been carried out using impact modifiers with successful outcomes (Afrifah and Matuana 2010; Balakrishnan et al. 2012; Notta-Cuvier 2014). PLA can be degraded by random hydrolysis of its ester bonds which decreases the molecular weight followed by reduction in mass loss. During degradation, it forms lactic acid which increases the soil fertility and also lessen the cost of waste management (Gunatillake and Adhikari 2003; Tokiwa and Calabia 2007). It is not easily harmed by microbial attack; however, certain enzymes and bacteria can degrade PLA such

as *Amycolatopsis*, *Proteinase K* (Smith 2005; Tokiwa et al. 2009; Kawai 2010). PLA has attracted great interest in medical and pharmaceutical applications such as implantable devices for sutures, staples, drug delivery systems, artificial skins, and scaffolds (Patricio et al. 2013; Fiori 2014). Aside from medical uses, it has been extensively used in daily life applications such as food packaging, household products, agricultural mulch films, textile and fibre industry, electrical appliances, automotive sector, and home/office furnishing products (Huda et al. 2008; Fiori 2014).

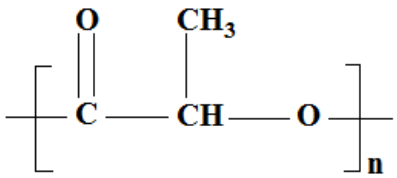


Figure 2.4. Chemical structure of PLA (adapted from Averous and Pollet 2012).

PCL is a petroleum-based aliphatic polyester and a biodegradable polymer. It is produced from cyclic monomer ε-caprolactone by ring-opening polymerization. The chemical structure of PCL is shown in Figure 2.5. It is among the most hydrophobic biodegradable polymers, and is non-toxic and mechanically strong as it possesses high flexibility and ductility. It has very low degradation rate as compared to PLA. Therefore, it is mostly used in biomedical applications such as drug delivery systems and tissue engineering (scaffolds). Moreover, it is also used in production of compostable bags for yard waste, food packaging, disposable food items, adhesives, and for agricultural mulch films. However, some drawbacks are also associated with PCL; it has low melting point and high cost (Gunatillake and Adhikari 2003; Elzubair et al. 2006; Auras et al. 2010; Liu and Zhang 2011; Abdolmohammadi et al. 2012; Patricio et al. 2013; dos Santos Rosa and Lenz 2013). Some extracellular enzymes and bacteria can degrade PCL such as *Proteobacteria, Penicillium sp.* (Tokiwa et al. 2009; dos Santos Rosa and Lenz 2013).

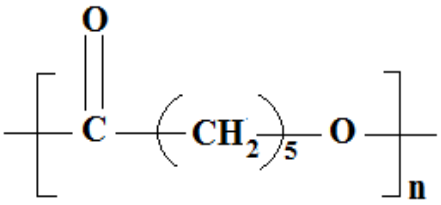


Figure 2.5. Chemical structure of PCL (adapted from Averous and Pollet 2012).

PLA and PCL are biodegradable polymers which can be subjected to various processing techniques such as extrusion, injection molding, compression molding, and solvent casting. Suitable curing methods can be used depending upon the biocompatibility and bioproduct formation (Gunatillake and Adhikari 2003). The comparable properties of PLA and PCL with PP are shown in Table 2.1.

Table 2.1. Properties of polylactic acid (PLA), polycaprolactone (PCL), and polypropylene (PP) based on the literature review (Faisant et al. 1998; Gunatillake and Adhikari 2003; Karnani et al. 1997; Maier and Calafut 2008; Murphy 2011; Reddy et al. 2013; Soleimani et al. 2008).

Polymer	**Tensile Modulus** (GPa)	**Melting Point** (°C)	**Melt Flow Index** (g/10min)	**Glass Transition Temperature** (°C)
Poly (*l*-lactic acid)	2.7	173 – 178	10 - 25 (@210°C/2.16 kg)	60 to 65
Poly(caprolactone)	0.4	58 – 63	3 (@160°C/2.16 kg)	-65 to 60
Polypropylene	0.69-1.2	130 - 170	18.6 – 21 (@230°C/2.16 kg)	-35 to 26

It can be seen from the table that mechanical properties of PLA are almost similar to the petrochemical polymer PP. Therefore, PLA has attracted great interest in replacing petroleum

based polymers. PCL has some similar mechanical properties as PLA; however, low glass transition temperature and low melting point could reduce its usage in some fields. Also, the degradation time for PLA and PCL has been determined to exceed 24 months without any environmental pollution, which will be helpful in producing biocomposites with longer life (Gunatillake and Adhikari 2003).

2.3 Manufacturing of biocomposites and study of their properties

Various methods have been studied with different biodegradable polymers to produce biocomposites. Soleimani and co-workers (2008) investigated the effect of fibre pretreatment and compatibilizer on the mechanical and physical properties of flax fibre polypropylene composites with compression molding technique. They used fibres treated with sodium hydroxide and mild bleach, and untreated fibre in the formulations. To study the effect of compatibilizer, maleic anhydride grafted polypropylene was added. The results showed that untreated fibres had shown inferior physical and mechanical properties than the treated ones. Also, the use of compatibilizer had some negative effects on the physical properties like color and melt flow index (Soleimani et al. 2008). Flax fibre polyethylene biocomposites were studied by Li and co-workers (2009) and reported that flax fibres which have shives had no difficulties in extrusion compounding and injection molding processing. The surface modification of flax fibres has successfully improved the interfacial bonding between polymer matrix and fibres and resistant towards water absorption in composites. The mechanical property, tensile strength increased with increase in flax fibre content up to a certain limit; but with greater fibre loading, moisture absorption resistance decreased (Li et al. 2009). The mechanical properties of treated and untreated flax fibres have also been studied with epoxy resin film as a matrix and it was observed that composites flexural properties were improved by treatment with alkali and dilute epoxy (Weyenberg et al. 2003).

Biodegradable PLA and PLA-PCL biocomposites were studied to investigate the effect of PCL on the fracture mechanism of the blend composite. The fracture energy increased with the use of PCL with other additives (Todo and Takayama 2011). The PLA/PCL scaffolds were formed by extrusion process and showed that it did not influence the thermal properties; however, melt blending process for scaffolds showed an increase in the mechanical properties (Patricio et al. 2013). The thermomechanical properties of oat hull reinforced PP/PLA composites were studied by varying composition of PP/PLA with oat hull fibres. Effect of thermal degradation, compatibilizer, crystallization, and interfacial adhesion were studied. The results showed that thermogravimetric analysis of oat hulls fibres was acceptable at 190 °C; thereafter, the oat hull composites lose weight with increased temperature. The mechanical properties revealed that the PP/PLA blend with oat hulls showed slightly higher tensile and flexural properties than PP-oat hulls matrix only; on the other hand, tensile and flexural properties considerably improved with the use of compatibilizer (Reddy et al. 2013).

The effect of chemical treatments on the mechanical properties and dimensional stability of cellulosic fibre-thermoplastic composites have shown improved physical and mechanical properties under extreme conditions, after which it was recycled (Karnani et al. 1997). To increase the adhesion properties of the fibre-matrix composite, chemical modification of natural fibres has been done by using chemical coupling agents which react with the hydroxyl group of cellulose and then react with the functional groups of the matrix (Bledzki and Gassan. 1999).

2.4 Summary

From the literature review, various studies were conducted on the extraction of natural fibres and modification in polymer matrix with biodegradable polymer. The physical, mechanical, and

thermal properties of different biodegradable materials were studied with modification of matrix by using various chemical and physical treatments.

Fibre extraction from oat hulls was investigated using dilute acid hydrolysis to extract the hemi-cellulose hydrolysate rich in xylose for the production of xylitol (Soleimani 2013). The by-product from oat hull hydrolysis composed of cellulose and lignin, has been investigated to develop biocomposites containing a PP polymer. However, investigation on the biocomposites from oat hull fibres and biodegradable polymers such as PLA and PCL remain relatively unexplored. Various studies have been conducted on different agricultural fibres such as flax fibres with PLA and PCL so that they could be used in biomedical applications, for example, in tissue engineering for making scaffolds, drug delivery systems, special packaging, and many other uses. On the other hand, PLA and PCL have poor thermal and mechanical properties as compared to PGA (polyglycolic acid). Still, PLA and PCL offer numerous advantages over the use of PGA since they are very low cost and have longer degradation period (almost doubled) compared with PGA. Moreover, fibres obtained from lignocellulosic biomass can degrade at high temperatures such that the processing should not exceed 200°C (Li et al. 2007). Due to this limitation of lower processing temperature, PLA and PCL polymers have been chosen to be paired with oat hull fibres for the development of biocomposites.

Therefore, the research plan was to develop eco-friendly composites from oat hulls with PLA and PCL, and to investigate their physical and mechanical properties by varying the ratios of AHB (acid- catalyzed hydrolysis by-product), CRB (cellulose rich biofibres), and chemically modified CRB fibres in the polymer matrix.

3. MATERIALS AND METHODS

This chapter contains the methodology of the research with description of materials and equipment, experimental procedures, data accumulation, and analysis to accomplish the objectives outlined in Chapter 1.

3.1 Overview of the research plan

The experimental plan for the production of biocomposites is shown in the flowchart in Figure 3.1. The biocomposites were developed and investigated by following a step-by-step procedure starting from the oat hull fibre preparation by physical and chemical treatments, mixing with biodegradable polymers, extrusion and compression molding, and finally, the physical and mechanical characterization of the biocomposites.

3.2 Materials

Oat hull biomass was supplied by Richardson Milling Ltd., Martensville, SK, Canada and its average density was measured to be 1.290 g/cm^3. Polylactic acid (PLA) powder (Ingeo Biopolymer 2003D) was obtained from NatureWorks LLC (Minnetonka, MN) and polycaprolactone (PCL) with trade name CAPA 6506 was purchased from Perstorp Polyols Inc. (Toledo, OH) in powder form. The impact modifier, Biomax Strong 120 (BS), an ethylene copolymer was purchased from DuPont Company (Wilmington, DE). Other chemicals such as sulfuric acid and sodium hydroxide were supplied by Fisher Scientific (Ottawa, ON).

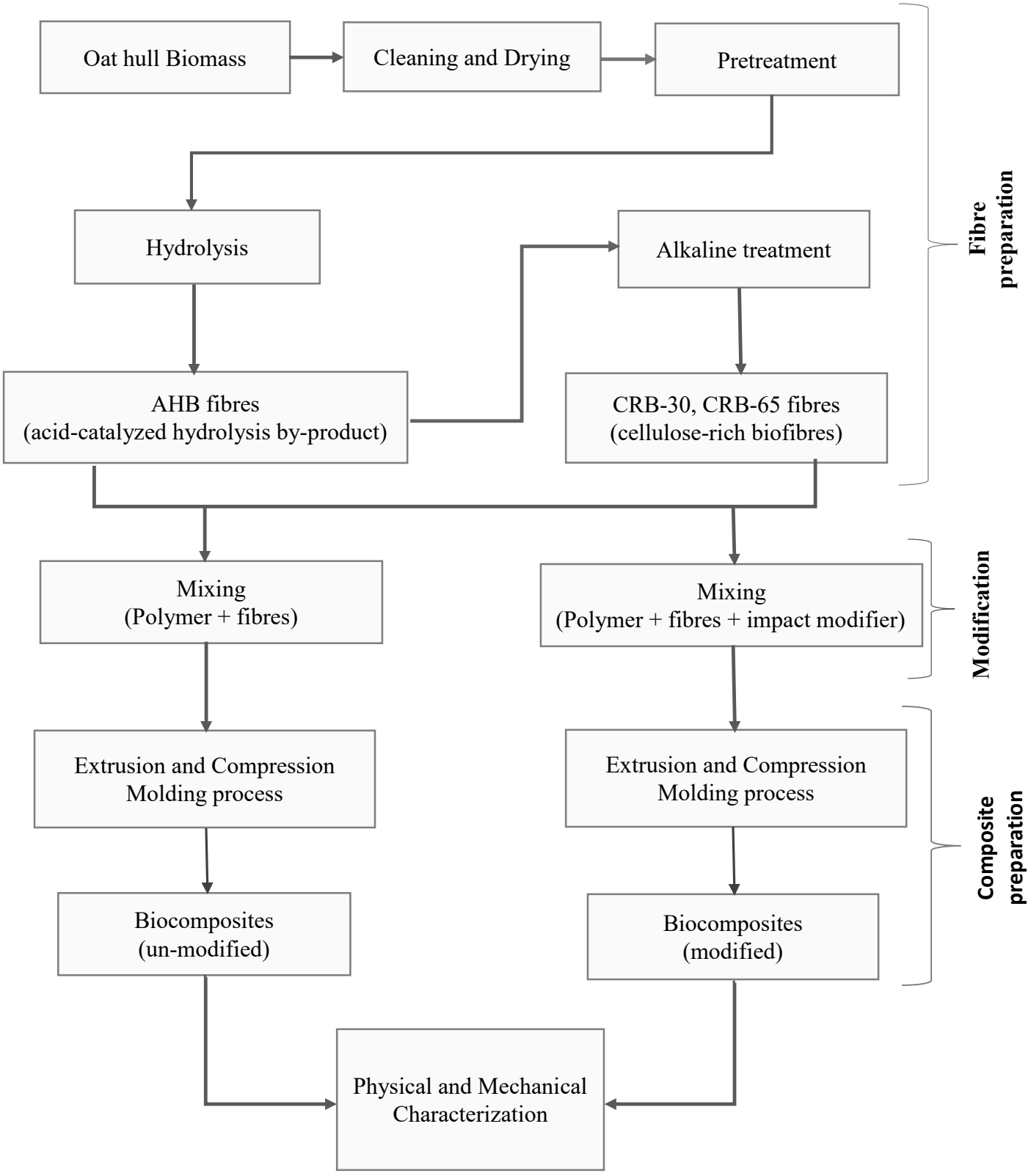


Figure 3.1. Flowchart for the experimental process of oat hull biocomposites.

3.3 Cleaning and size reduction of oat hulls

The original raw material (oat hulls) was cleaned using a sieving machine (Link Manufacturing Company Inc., Fargo, ND) and then passed through an aspirator where the hulls were separated from whole grains and fines.

The sieving machine and aspirator used to clean oat hulls are shown in Figure 3.2 and 3.3, respectively. The raw material as obtained from Richardson Milling Ltd. Company is shown in Figure 3.4. The unwanted material from the oat hulls was removed and the cleaned hulls were obtained as displayed in Figure 3.5.

The cleaned hulls were then ground through a 2.7 mm opening sieve using a grinder mill (Retsch GmbH 5657 HAAN, West Germany) as shown in Figure 3.6 and the ground hulls are shown in Figure 3.7.

Figure 3.2. Sieving machine used to clean biomass.

Figure 3.3. Laboratory scale aspirator.

Figure 3.4. Original raw material (oat hulls) before cleaning.

Figure 3.5. Cleaned oat hulls.

Figure 3.6. Grinder mill for size reduction of biomass.

Figure 3.7. Ground oat hulls.

3.3.1 Initial moisture content of oat hulls

The moisture content of oat hulls was determined by ASAE S358.2 standard (ASABE 1993) which was developed by American Society of Agricultural and Biological Engineers (ASABE) for forage crops. A sample of 25 g was taken and dried in an oven at 103°C for 24 h. After drying, the percent moisture content was calculated on wet basis (M.C. %w.b.). The moisture content values of raw material (hulls + endosperm grits), cleaned hulls, and ground hulls are given in Table 3.1 on percent wet basis.

Table 3.1. Moisture content (%w.b.) of the original and the cleaned/ground materials.

Material	Original raw material	Cleaned Hulls	Ground Hulls
M.C. (%w.b.)	11	10	8.6

3.3.2 Yield of cleaned oat hulls

The results after sieving/cleaning for the hulls and the impurities (fines, grains), and also losses are tabulated in Table 3.2 on percentage basis. The fraction removed after cleaning of the hulls was 44 % in total and was rich in fines, whole grains, and broken kernels. The total recovery of cleaned hulls was 52%.

Table 3.2. Hulls, fines, and grains content in the original oat hull.

Material	Hulls	Fines	Grains	Losses
Content (%)	52	39	5	4

3.4 Fibre preparation

The ground portion of the hulls was then subjected to the hydrolysis with dilute sulfuric acid treatment to get fibres rich in cellulose and lignin, which was followed by alkali treatment with sodium hydroxide for the delignification of the fibres.

3.4.1 Dilute acid hydrolysis

The ground hulls were pretreated by dilute acid hydrolysis under atmospheric conditions, with 1.2N H_2SO_4 (sulfuric acid) under continuous stirring for 80 min. The hydrolysis set-up for the pretreatment of ground oat hulls is shown in Figure 3.8. The apparatus for hydrolysis consisted of a 2 litre glass beaker which was covered with a silicone lid and attached to a condenser for reflux. The inside temperature of the mixture was maintained by inserting a temperature probe which was connected to the temperature controller. The hydrolysis experiments were carried out at temperature of 99°C and agitation speed of 300 rpm with solid to liquid ratio of 1:10 (w/w), respectively. Afterwards, mixture was washed with distilled water to neutralize the pH. The solid fraction obtained after filtration was the acid-catalyzed hydrolysis by-product (AHB) and, it was

then air dried in an oven (LDB-1-67, Despatch Industries, Minneapolis, MN) at 60°C for 48 h. The AHB fibres recovered after hydrolysis (Figure 3.9) were rich in cellulose and lignin with higher percentage of cellulose.

Figure 3.8. Hydrolysis set-up for the pretreatment of biomass.

Figure 3.9. Acid-catalyzed hydrolysis by-product (AHB fibres) obtained after hydrolysis.

3.4.2 Delignification

Delignification was done on AHB fibres by alkaline treatment for the removal of lignin and to convert it to cellulose-rich biofibre (CRB). The procedure followed was based on literature review and the temperatures of 30°C and 65°C were adopted for delignification of AHB fibres based from previous work in our research group (Soleimani and Tabil 2012; Soleimani 2013). AHB fibres were treated with 5% (w/w) NaOH solution at 30°C and 65°C, in a glass container with reflux and continuous stirring for 2 h. The same experimental set-up used for hydrolysis, was also used in delignification process. After thorough washing and drying, the solid fractions obtained at two treatment temperatures (30°C and 65°C) are called as cellulose-rich biofibres, namely CRB-30 and CRB-65. These CRB fibres were dried for 48 h in an oven at 60°C and are shown in Figure 3.10.

Figure 3.10. Cellulose-rich biofibres (CRB) obtained after alkaline treatment.

3.4.3 Yield of AHB, CRB-30 and CRB-65 fibres

The solid fractions obtained after dilute acid hydrolysis and delignification, where three different fibres were obtained; AHB, CRB-30 and CRB-65. After drying, the yield (%) of AHB from the initial raw material hydrolyzed, and of CRB-30 and CRB-65 from the delignification of AHB fibres are presented in Table 3.3, respectively. The yield of the AHB fibres after dilute acid hydrolysis was 41%; on the other hand, after delignification of AHB fibres at two different temperatures of 30°C and 65°C, the yield of recovered CRB-30 and CRB-65 fibres was 75% and 65%, respectively.

Table 3.3. Yield (%) of acid-catalyzed hydrolysis by-product (AHB) and cellulose-rich biofibres (CRBs) after drying.

Fibre type	AHB	CRB-30	CRB-65
Yield (%)*	41	30.75	26.65

* Yield in percent of the initial cleaned hull sample.

3.5 Formulations and mixing

After pretreatment, three different types of fibres namely, AHB, CRB-30, and CRB-65 were ready for formulations and mixing with two different biodegradable polymers, i.e. PLA and PCL, and impact modifier. The fibres and polymers were dried first to reduce the moisture content before mixing.

The formulations for composites were prepared in two manners:

1) without impact modifier / Un-modified (shown in Table 3.4); and
2) with impact modifier (BS) / Modified (shown in Table 3.5)

Impact modifier, Biomax Strong 120 (BS), is a petroleum-based ethylene acrylate copolymer which is known to be compatible with PLA and mostly used to improve the impact properties of PLA (Talimi 2011).

Fibre loading used in both formulations at levels of 15% and 30% (w/w) was chosen, based on previous research findings of our research group (Soleimani et al 2008; Soleimani and Tabil 2012). The inclusion rate of impact modifier, Biomax Strong 120 (BS) in modified biocomposites was taken 15% (w/w) in this study as per literature review (Afrifah and Matuana 2010). Virgin PLA and PCL samples were made as reference materials with 0% fibre content. The different formulations were mixed by a blender before extrusion in order to achieve homogenous mixture of fibres and polymers.

Table 3.4. Formulation of composites based on polymer matrix and fibres derived from oat hull.

Polymer	Fibre	Formulation (%)
		Polymer/fibre
PLA	-	100/0
	AHB	85/15
		70/30
	CRB-30	85/15
		70/30
	CRB-65	85/15
		70/30
PCL	-	100/0
	AHB	85/15
		70/30
	CRB-30	85/15
		70/30
	CRB-65	85/15
		70/30

Table 3.5. Formulation of composites based on polymer matrix, cellulose-rich biofibres (CRB), and impact modifier (BS).

Polymer	BS-Fibre	Formulation (%)
		Polymer/BS/fibre
PLA	-	100/0
	BS-CRB-30	70/15/15
		55/15/30
	BS-CRB-65	70/15/15
		55/15/30
PCL	-	100/0
	BS-CRB-30	70/15/15
		55/15/30
	BS-CRB-65	70/15/15
		55/15/30

3.6 Composite preparation

Biocomposites were prepared by using extrusion and compression molding techniques which are discussed below.

3.6.1 Extrusion compounding

A twin screw extruder (SHJ-35, Nanjing Yongteng Chemical Equipment Co. Ltd., Jiangsu, China) was used to extrude the formulations as shown in Figure 3.11. The formulations were fed into the hopper and controlled manually. The extruder was electrically heated and water cooled. It was also driven by variable screw speed which was adjusted according to the process. It was equipped with a temperature controller and all the temperatures were displayed during extrusion. There were 10 temperature zones starting from the feeding zone to the exit zone. The zones were subdivided into solid conveying, melting, mixing, and pumping zones. For PLA formulations, the extruder barrel zone temperatures were consistent from zone 1 to 10 at 145, 150, 155, 160, 165, 170, 170, 175, 180, and 185°C, and for PCL formulations at 50, 60, 70, 80, 80, 90, 100, 120, 120, and 120°C, respectively. The mixture was then extruded through a die consisting of four-holes and the extrudate strands were cooled in water bath right after exiting the die. The solidified strands were then air dried by a fan and pelletized using pelletizer mill as shown in Figure 3.12. The compounded pellets for composite preparation are shown in Figure 3.13.

Figure 3.11. Twin-screw extruder used in compounding biocomposite formulations.

Figure 3.12. Blow drying fan and pelletizer mill.

Figure 3.13. The pelletized extrudate after cutting.

3.6.1.1 Extrusion methodology

Extrusion is a process in which continuous melting, mixing, and shaping of polymer matrix take place. The polymer matrix (or input material) with uniform cross-sectional area continuously flow through an orifice of suitable die tool and consequently solidification of the output material occurs in extrusion (Rosen 1971; Charrier 1991; Strong 2006).

It is the most common and efficient method for the production of composites with thermoplastic polymers. Two major advantages of extrusion are that it can continuously manufacture high production volumes and has the flexibility to process brittle materials (Strong 2006; Talimi 2011). The compounding of polymer with fibrous materials and additives is used to modify engineering properties of materials (Siaotong 2006). Moreover, extrusion helps to achieve proper dispersion of fibres into the polymer matrix (Panigrahi et al. 2003).

Extrusion can be done through a single-screw extruder or twin-screw extruder. In this study, a twin screw extruder was used for the compounding purposes as compared to single screw extruder. Twin-screw extruder is known to give better fibre dispersion as the shear force between both screws provide intimate mixing between fibre and polymer matrix (Pickering et al. 2015). In addition, this type of extruder is valuable for processing of temperature sensitive polymers (Strong 2006).

A schematic diagram of full extrusion process is given in the Figure 3.14. The material or formulations were fed into the feeder attached to the extrusion machine. The material then passed through a hole and fell onto the extrusion screw. The extrusion screw inside the barrel zone conveyed the material into the heated zones, where melting, mixing, and pushing of the polymers and fibres had taken place from zone 1 to zone 10. The temperature at the beginning of the first zone was kept lower and then started increasing in the proceeding zones. The temperatures were kept constant in each zone and controlled by temperature controller. The conveyed material was then passed through the die attached at the end of the extruder barrel. The extrudate strands were extruded through four-hole die (tool) and immediately cooled in the water bath. The solidified strands were then blow dried by a fan installed next to water bath. The dried strands were then pelletized using a pelletizer mill.

The extruder was purged with the virgin polymer so that formulations were identified alternatively, after each sample exiting the die.

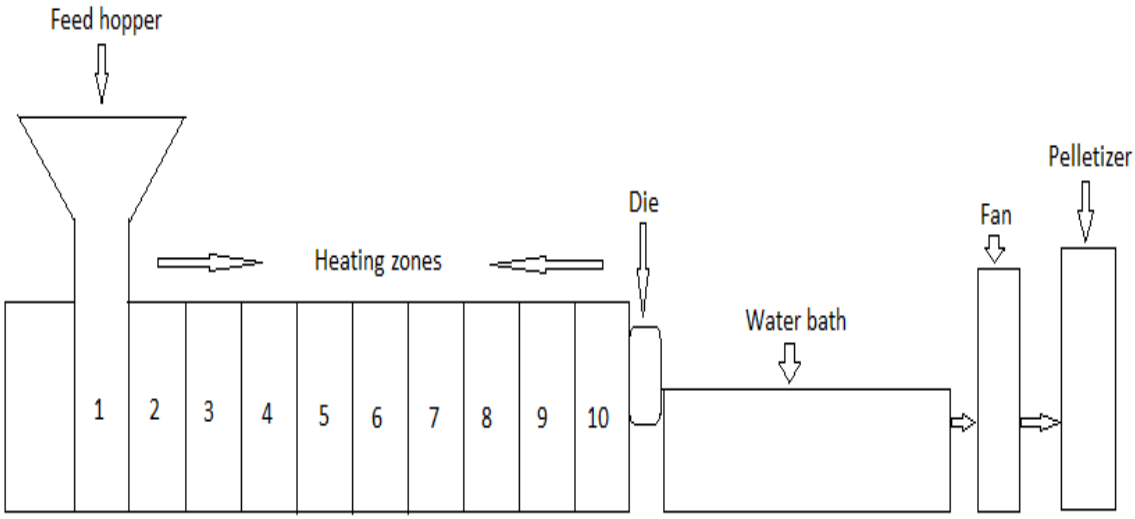


Figure 3.14. Schematic diagram of the biocomposite extrusion process.

3.6.2 Drying

The pelletized material was then dried in an oven at required temperatures depending on the type of formulation. This was done in order to remove any possible moisture left in the pelletized material and to avoid any void formation in the final product from compression molding.

3.6.3 Compression molding

Compression molding technique was used for the preparation of biocomposite sheets from the pelletized material. The compression molding machine was made of hand-operated hydraulic press (Miller Machine Tools, J.B. Miller Machinery & Supply Co. Ltd., Toronto, ON) shown in Figure 3.15. The two adjustable features in this press were temperature and pressure. A temperature probe was also used to measure the inside temperature of the sample. The processing temperatures and pressures for PLA and PCL composites were identified based on some preliminary experiments and literature review. A rectangular mold was used to prepare sample sheets of 200 mm × 200 mm

in size. The outside parts of the mold were made up of construction grade steel, while the inside parts were of aluminium, as shown in Figure 3.16.

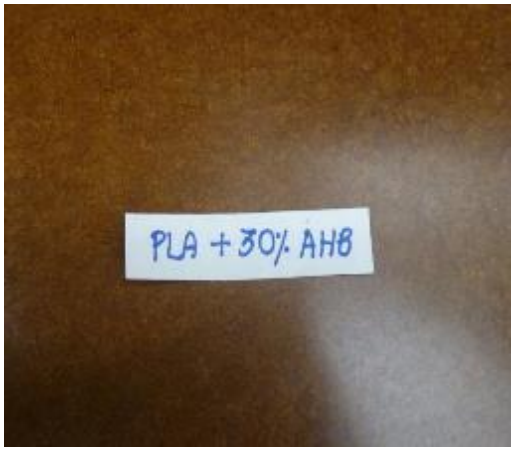
Figure 3.15. Compression molding machine.

Figure 3.16. Molds (of aluminium and construction grade steel) used to produce composite sheets.

The upper and lower plates of the compression molding machine were heated and the temperature was adjusted depending on the type of polymer matrix. Thereafter, the pelletized material was loaded into the designed mold and machine was full-pressed under required pressure for a desired period of time. The sheets were cured by water-cooling system installed in the machine. After cooling, the material was solidified and demolded.

The biocomposite sheets developed from different formulation compression molding are shown in Figure 3.17. The sheets were cut off into desired specimens for physical and mechanical tests according to the ASTM standards.

(a)



(b)

(c)

Figure 3.17. Biocomposites with different formulations of PLA and fibres after compression molding.

3.6.3.1 Compression molding methodology

Compression molding is the oldest manufacturing method in the plastic manufacturing industry (Mallick and Newman 1990). It is a batch process, in which products are made one at a time (Powell 1983). Traditionally, it was used for thermosetting materials. But with recent developments in advanced thermoplastic composites, it has been very popular in the development of natural fibre composites (Mallick and Newman 1990; Talimi 2011; Faruk et al. 2012). The processing of thermoplastics is different from thermosets as the thermoplastics are formed by heating above their melting point and then cooled down (Talimi 2011; Salit 2014). It is a high-pressure plastic molding method which is used to produce complex and high strength components, for example in the production automotive parts. Other advantages associated with this method are its high reproducibility and low cycle time (Talimi 2011; Faruk et al. 2012; Salit 2014).

In this method, open molds were used in a pair, called as top mold and bottom mold as shown in the schematic view of Figure 3.18. The charge or material around 150g was first weighed to prevent excess flash. Then, the charge was placed into the bottom mold and it was covered up by top mold. The mold was then hydraulically pressed in the compression molding machine which was electrically heated. The material started melting in order to regain the shape of the mold. Temperature and pressure were the key parameters in the production biocomposites. The PLA composites were pressed at temperature of 190°C and pressure of 31.14 kN. For PCL composites, the compressed pressure was 31.14 kN with 85°C of temperature. The molding process took up to 15 min for the sheet formation. Later, the mold was cooled and biocomposite sheets were withdrawn.

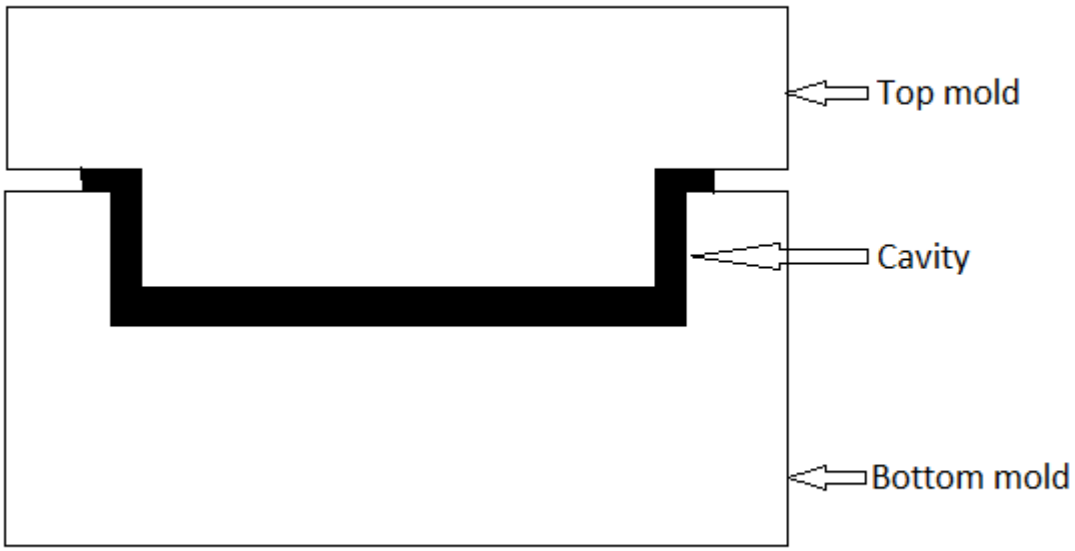


Figure 3.18. Schematic diagram of compression mold.

3.7 Characterization: Physical and Mechanical Properties

To study the physical and mechanical properties of the molded biocomposites from PLA and PCL formulations, various tests were conducted in accordance with ASTM and ISO standards. The physical tests focused on the measurement of color, density, and water absorption in the developed composites. The mechanical tests targeted on the tensile, flexural, and impact properties of the biocomposites. Each mechanical test was carried out with 10 replicates for each formulation type of PLA and PCL. During physical tests, triplicate measurements were chosen for all above mentioned tests.

3.7.1 Color measurement

Color measurement was done to analyze the degree of degradation in the biocomposite components during processing i.e. extrusion and compression molding. The effect on the

appearance of molded composites, developed with addition of acid treated and alkaline treated fibres and due to temperature and pressure conditions was analyzed by HunterLab ColorFlex EZ spectrophotometer (Hunter Associates Laboratory, Inc., Reston, VA) which is shown in Figure 3.19. The Hunter L*, a*, and b* color coordinates were used for color measurement, where L* is the whiteness component and a* and b* are both chromatic components with a* from green to red and b* from blue to yellow. Equations 3.1, 3.2 and 3.3 are used to illustrate the meaning of L*, a* and b* respectively. The difference between the L*, a*, and b* color coordinates of the sample composites and virgin polymer (PLA or PCL) was used to calculate color index, ΔE which is highly dependent on ΔL*, as shown in the equation 3.4 (Soleimani et al 2008; Soleimani and Tabil 2012).

$$L^* = 0(black) \;\; to \;\; 100(white) \tag{3.1}$$

$$a^* = \; -a^*(green) \;\; to \;\; +a^*(red) \tag{3.2}$$

$$b^* = \; -b^*(blue) \;\; to \;\; +b^*(yellow) \tag{3.3}$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{3.4}$$

where: $\Delta L^* = L^*_{sample} - L^*_{virgin}$, $\Delta a^* = a^*_{sample} - a^*_{virgin}$, $\Delta b^* = b^*_{sample} - b^*_{virgin}$.

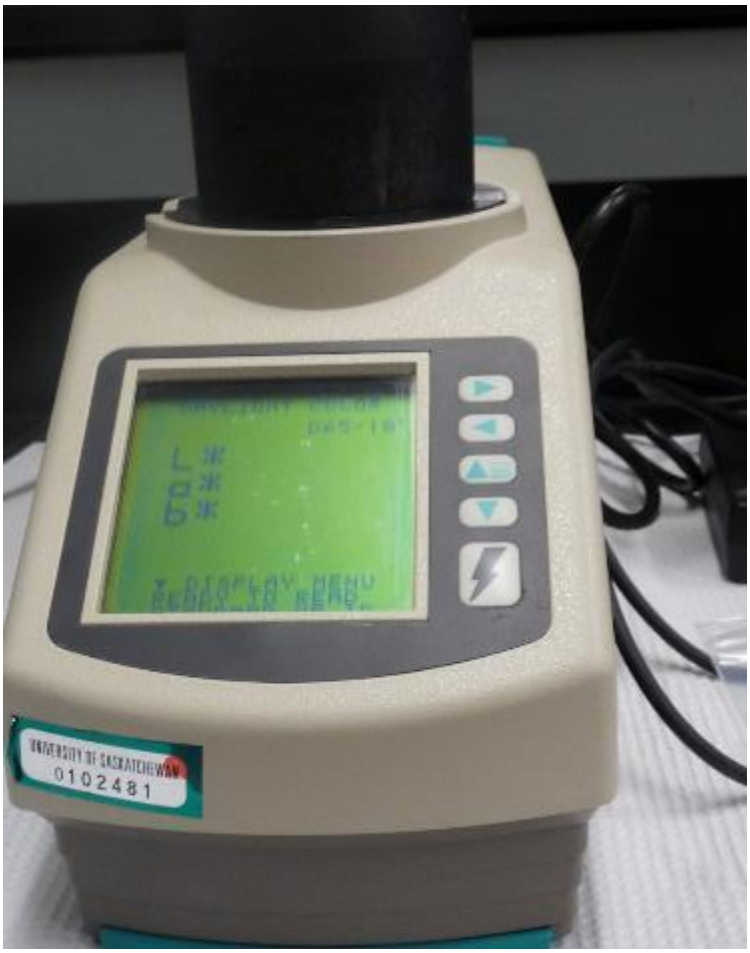


Figure 3.19. HunterLab ColorFlex EZ spectrophotometer.

3.7.2 Density test

The density of composites is defined as the mass per unit volume and is expressed in grams per cubic centimeter. The mass of the samples was measured in grams using a weighing scale (OHAUS Scale Corporation, Florham Park, NJ). The volume of the samples was measured by using a pycnometer as shown in Figure 3.20, which was operated by nitrogen gas (Quantachrome Corporation, Boynton Beach, FL) and density of the samples was calculated by dividing the mass by the volume.

Figure 3.20. Pycnometer (gas-operated) for volume measurement.

3.7.3 Water absorption test

ASTM test method D570 (Standard test method for water absorption of plastics) (ASTM 2010) was followed for the water absorption of biocomposites. The test specimens with thickness of 3mm were cut into rectangular shapes with dimensions of 76.2 mm in length and 25.4 mm in width. The specimens were then dried in an oven at 50°C for 24 h, cooled in a desiccator, and weighed immediately to the nearest 0.001 g (dried weight = W_{dried}). The dried specimens were immersed in water for the next 24 h at room temperature of 23°C as shown in Figure 3.21, and weighed again after wiping off excess water from the surface with a dry cloth (wet weight = W_{wet}). The percent increase in weight was calculated by equation 3.5:

$$Water\ absorption\ (\%) = \frac{W_{wet} - W_{dried}}{W_{dried}} \times 100 \qquad (3.5)$$

Figure 3.21. Water absorption measurement.

3.7.4 Tensile test

The tensile test of biocomposites was carried out by using Instron universal testing machine (INSTRON 3366, Instron Corp., Norwood, MA). Specimens in a dog-bone shape were prepared with dimensions of 196 mm (overall length), 22 mm (overall width), and 3 mm (thickness), from the biocomposite samples according to the ASTM standard test method D638 (ASTM 2014) as shown in Figure 3.22. The tensile test was performed on INSTRON 3366 (Figure 3.23), at crosshead speed of 5 mm/min and two important properties, tensile strength (σ_t, MPa) and Young's modulus (E, GPa) were calculated using equations 3.6 and 3.7, respectively.

$$\sigma_t = \frac{F_{max}}{A} \tag{3.6}$$

$$E = \frac{\sigma}{\varepsilon} \tag{3.7}$$

Where F_{max} is the maximum load (N); A, cross-sectional area (mm^2); σ, tensile stress (MPa); and ε, extensional strain.

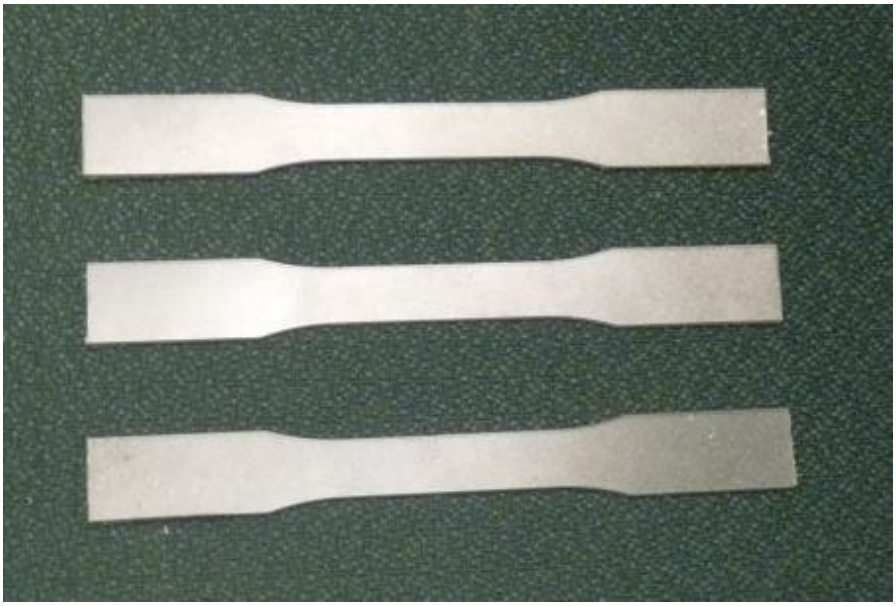


Figure 3.22. Dog-bone shaped specimens for tensile test (from virgin PLA compression molded sheet).

Figure 3.23. Universal testing machine (INSTRON 3366) used to perform tensile test.

3.7.5 Flexural test

The flexural properties of acid treated and alkaline treated composites were determined as described in ASTM D790-10 (Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials) (ASTM 2010). Specimens were cut into dimensions of 12.7 mm (width) and 127 mm (length) with 3 mm (thickness). The test specimens were conditioned in an environment chamber at 23 ± 2°C and 50 ± 5 % relative humidity for more than 40 h before testing (BRYANT Manufacturing Associates, Ayer, MA) (Figure 3.24). Three-point bending test was performed on all the specimens by using Instron universal testing machine (INSTRON 3366) (*cf.* Figure 3.25 and 3.26) with crosshead speed of 5 mm/min and length between

support span of 48 mm. Flexural strength (σ_f, MPa) and flexural modulus (E_f, GPa) were calculated using equations 3.8 and 3.9, respectively. The schematic diagram of flexural test is shown in Figure 3.27.

$$\sigma_f = \frac{3PL}{2bd^2} \tag{3.8}$$

$$E_f = \frac{mL^3}{4bd^3} \tag{3.9}$$

Where P is the maximum load (N); L, length between support span (mm); b, width of the specimen (mm); d, thickness of the specimen (mm); and m, slope of the load-displacement curve.

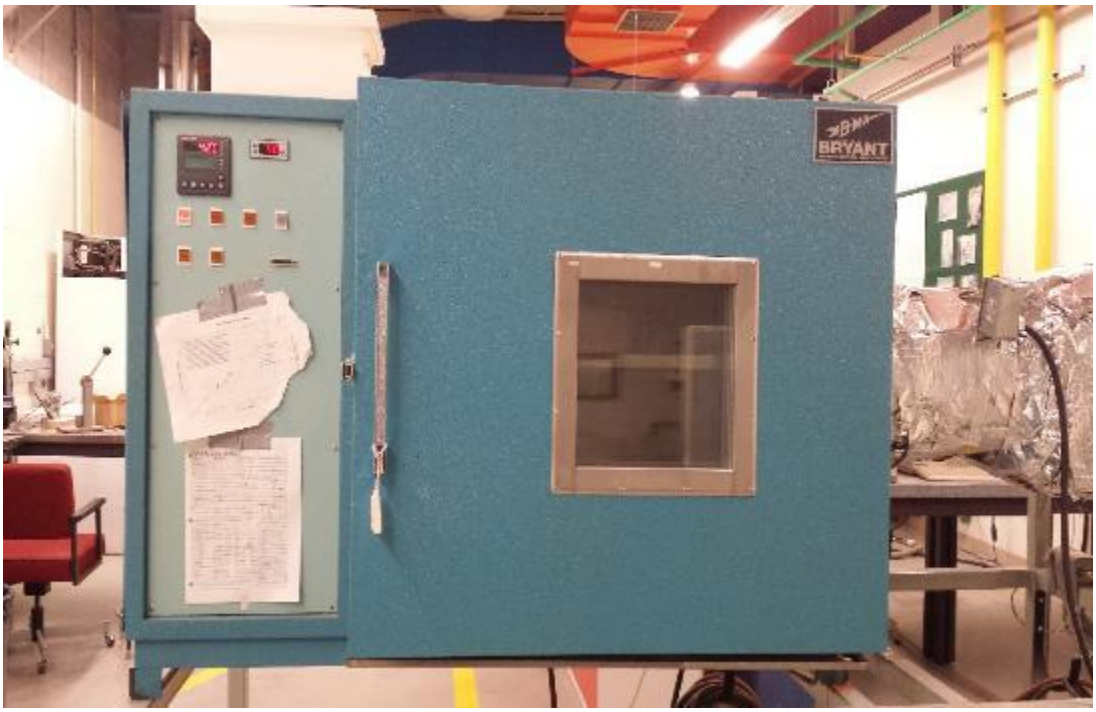


Figure 3.24. Environmental chamber for conditioning of the biocomposites.

Figure 3.25. Flexural testing using INSTRON 3366 universal testing machine.

Figure 3.26. Magnified view of the three-point bending test using a test specimen.

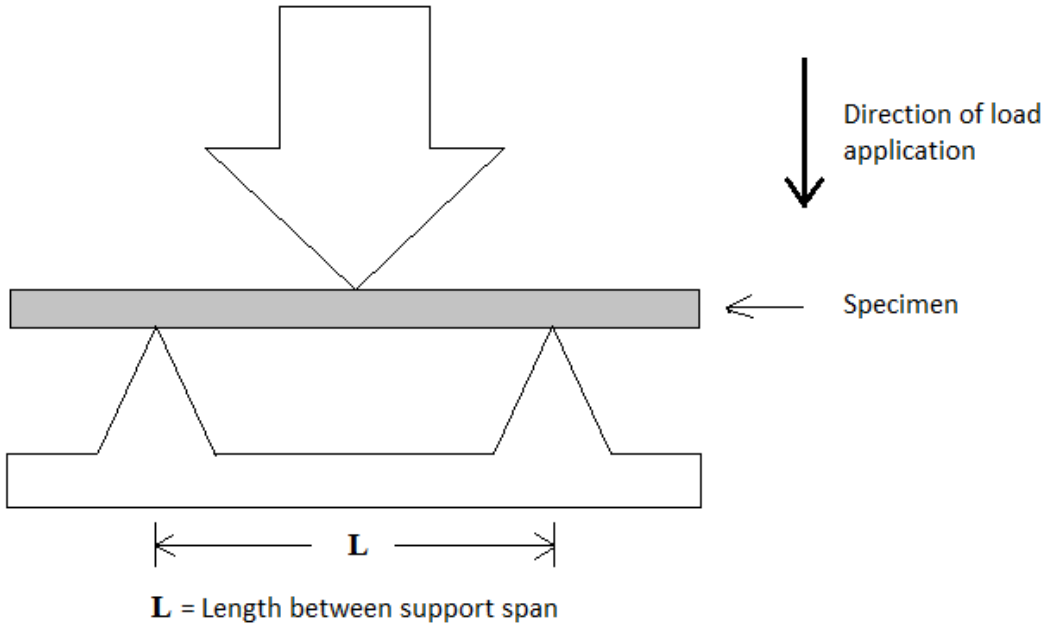


Figure 3.27. Schematic view of flexural test.

3.7.6 Tensile-impact test

Toughness of the polymeric materials can be determined by measuring impact properties. The higher is the impact energy of the material, higher is the toughness. According to ISO Standard 8256, tensile-impact strength is the energy absorbed in breaking a specimen under specified conditions, referred to the original cross-sectional area of the specimen. The test was conducted using a tensile-impact testing machine (Tinius Olsen Testing Machines Co., Willow Grove, PA) as shown in Figure 3.28. The test specimens with dimensions of 80 mm (length), 3 mm (thickness), and 10 mm (width) were made as stated in ISO 8256 standard (ISO 2004) and clamped to the pendulum. The test specimen was broken by a single impact at the bottom of the swing of the pendulum and tensile-impact energy (kJ/m^2) was calculated as using equation 3.10.

$$a_{tu} = \frac{E_i}{x \times h} \tag{3.10}$$

Where α_{tu} is the tensile-impact strength in kJ/m^2; E*i*, impact energy in J; x, width of the sample in mm; and h, thickness of the sample in mm.

Figure 3.28. Tensile-impact test apparatus.

3.7.7 Compositional analysis

The ground hulls (raw material) and recovered fibres (AHB, CRB-30, and CRB-65) were analyzed to determine the proportions of cellulose, hemi-cellulose and lignin. Association of Official Analytical Chemists (AOAC) standards No. 2002.04 (AOAC 2005) and No. 973.18 (AOAC 1997) were used for NDF and ADF measurements to determine the contents of hemi-cellulose and cellulose, respectively. The percentage of lignin was measured by National Renewable Energy Laboratory (NREL) standard No. 03 (Sluiter 2008).

In NDF (neutral detergent fibre) method, neutral detergent and enzyme solutions were used to remove non-fibrous content by digestion and dissolution from the fibrous material. After that, the non-soluble part was filtered, thoroughly washed and dried. The dried sample was then incinerated to measure ash content, from which NDF value was calculated by difference in sample weight, between before and after treatment. In ADF (acid detergent fibre) method, a sample was weighed to nearest 1 g (approximately 0.9 to 1.1 g) and refluxed with 1.0 N sulfuric acid solution for 1 h. Thereafter, the sample was filtered, washed, and dried to determine ADF quantity, i.e. cellulose and lignin content. The lignin content was measured by NREL method, where the sample was predigested with 72% sulfuric acid and stirred every 15 min for 2 h at room temperature. Thereafter, the sample was boiled in 3% diluted sulfuric acid for 4 h under reflux condenser. Finally, the solid fraction was dried and lignin quantity was determined.

3.7.8 Data analysis

The data was analyzed by using SPSS statistical analysis software (IBM SPSS Statistics, IBM Corporation, New York, NY) on the basis of completely randomized design. Analysis of variance (ANOVA) was used to measure the difference between means, which were compared by using Duncan's multiple range test at 5% significance level.

4. RESULTS AND DISCUSSION

In chapter 3, experimental methods were discussed to manufacture biocomposites from biodegradable polymers and oat hulls. Tests were performed to determine the physical and mechanical properties of the developed composites with different inclusion rate of acid-catalyzed hydrolysis by-product and cellulose-rich biofibres. Experiments to study the effect of impact modifier on biocomposites were also conducted. In this chapter, the results of physical and mechanical properties are presented and discussed.

4.1 Chemical composition of oat hulls and fibres

The chemical compositions of raw oat hulls and its fibres namely, AHB, CRB-30, and CRB-65 before and after various stages of chemical modifications are presented in Table 4.1 and the values obtained are the average of the replicated measurements. The percentage of cellulose, lignin, and hemi-cellulose recovered in raw oat hulls is approximately 24.70, 17.70, and 39.33%, respectively. The data obtained after chemical treatments has resulted in the reduction of hemi-cellulose and lignin contents, with increased cellulose composition.

After acid hydrolysis, the hemi-cellulose content could be totally eliminated from the AHB fibres as indicated by data and consequently followed the same trend in delignified fibres, i.e. in CRB-30 and CRB-65. In the delignification process of AHB fibres, followed by increase in reaction temperature from 30 to 65 °C, has resulted in decrease of lignin to cellulose ratio from 0.53 in AHB, to 0.33 and 0.16 in CRB-30 and CRB-65, respectively. Therefore, cellulose content has been increased from 56.90% to 83.23% and lignin has been decreased from 30.24% to 13.55% from AHB to CRB-65, respectively.

Table 4.1. Percentage of cellulose, lignin, and hemi-cellulose in raw oat hulls and chemically modified fibres with corresponding standard deviation (SD).

Material	Cellulose (%)	SD	Lignin (%)	SD	Hemi-cellulose (%)	SD	Lignin/ Cellulose
RM	24.70*	±1.04	17.70	±0.72	39.33	±0.56	0.72
AHB	56.90	±1.31	30.24	±1.10	0	-	0.53
CRB-30	71.00	±1.53	23.81	±0.69	0	-	0.33
CRB-65	83.23	±1.02	13.55	±0.80	0	-	0.16

RM, raw material (oat hulls); AHB, acid-catalyzed hydrolysis by-product; CRB, cellulose-rich biofibre
*N = 3

4.2 Color

The color index (ΔE) values calculated for PLA- and PCL-based biocomposites are shown in Table 4.2. The results of this study are consistent with the previous studies in PP-flax fibre composites and PP-oat hull fibre composites (Soleimani et al. 2008; Soleimani and Tabil 2012). For molded virgin PLA, the L* value was the highest and a* and b* values were lowest, indicating that the molded PLA composites appeared darker with addition of fibre. The highest ΔE values for PLA were associated with acid treated composites, whereas the least ΔE values were seen in alkaline treated composites. PCL color measurements, also showed the lowest L* values and the highest a* and b* values for almost all the acid and alkaline treated molded composites than molded virgin PCL. The low L* values could be due to inclusion of fibres; but there was no degradation of fibres as per lower processing temperature conditions for PCL. However, no significant effect was observed by fibre loading in both formulations with PLA and PCL.

Furthermore, objective 3 was achieved with the addition of impact modifier to the PLA- and PCL-based composites with alkaline treated fibres only and the values for color index and color coordinates are shown on Table 4.3. Overall, for both PLA- and PCL-modified composites,

Table 4.2. Values of color coordinates and color index with standard deviation (SD) and comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d for PLA and A,B,C,D for PCL formulation type.

Polymer	Fibre	Formulation (%)	L*	SD_{L*}	a*	SD_{a*}	b*	SD_{b*}	ΔE	$SD_{\Delta E}$
		Polymer/fibre								
PLA	-	100/0	35.41	±0.36	-0.41	±0.07	10.96	±0.29	0^{d}	±0.00
	AHB	85/15	29.34	±0.22	10.58	±0.18	16.51	±0.34	21.29^{a}	±0.29
		70/30	28.89	±0.08	10.38	±0.25	16.23	±0.24	20.78^{a}	±0.27
	CRB-30	85/15	29.23	±0.42	8.74	±0.22	15.29	±0.74	19.39^{b}	±0.85
		70/30	28.39	±0.67	9.05	±0.99	15.02	±0.99	18.98^{b}	±1.54
	CRB-65	85/15	27.39	±0.19	8.69	±0.23	14.04	±0.26	17.64^{c}	±0.24
		70/30	28.12	±0.28	8.83	±0.17	14.41	±0.24	18.29^{b}	±0.40
PCL	-	100/0	59.33	±0.59	-0.69	±0.02	-1.09	±0.07	0^{D}	±0.00
	AHB	85/15	36.72	±0.14	10.14	±0.17	19.19	±0.14	32.25^{B}	±0.18
		70/30	34.87	±0.24	10.76	±0.34	18.98	±0.90	33.66^{A}	±0.56
	CRB-30	85/15	33.97	±0.57	8.67	±0.39	16.40	±0.42	32.21^{B}	±0.23
		70/30	34.17	±0.73	8.39	±0.31	16.18	±0.44	31.85^{C}	±0.35
	CRB-65	85/15	34.21	±0.10	8.35	±0.31	15.94	±0.21	31.67^{C}	±0.12
		70/30	33.12	±0.37	8.64	±0.22	17.05	±0.37	33.22^{A}	±0.30

SD_{L*}, standard deviation of L*; SD_{a*}, standard deviation of a*; SD_{b*}, standard deviation of b*; $SD_{\Delta E}$, standard deviation of ΔE

Table 4.3. Values of color coordinates and color index with standard deviation (SD) and comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c for PLA and A,B,C,D for PCL formulation type with chemical modifier (BS) and cellulose-rich fibres (CRB).

Polymer	Fibre	Formulation (%) Polymer/BS/ fibre	L*	SD_{L^*}	a*	SD_{a^*}	b*	SD_{b^*}	ΔE	$SD_{\Delta E}$
PLA	-	100/0/0	35.41	±0.36	-0.41	±0.07	10.96	±0.29	0^{c}	±0.00
	CRB-30	70/15/15	29.94	±0.27	9.27	±0.30	17.27	±0.27	21.46^{b}	±0.39
		55/15/30	32.09	±0.69	9.72	±0.23	17.70	±0.46	23.03^{a}	±0.78
	CRB-65	70/15/15	29.08	±0.17	9.19	±0.27	16.90	±0.14	20.76^{b}	±0.19
		55/15/30	29.73	±0.28	10.10	±0.03	18.06	±0.21	22.36^{a}	±0.29
PCL	-	100/0	59.33	±0.59	-0.69	±0.02	-1.09	±0.07	0^{D}	±0.00
	CRB-30	70/15/15	36.21	±0.12	7.76	±0.22	15.35	±0.45	29.60^{B}	±0.22
		55/15/30	34.93	±0.11	8.30	±0.06	16.60	±0.17	31.45^{A}	±0.12
	CRB-65	70/15/15	37.32	±0.39	7.14	±0.17	14.35	±0.21	28.01^{C}	±0.16
		55/15/30	33.63	±0.36	7.60	±0.11	15.01	±0.14	31.44^{A}	±0.21

SD_{L^*}, standard deviation of L*; SD_{a^*}, standard deviation of a*; SD_{b^*}, standard deviation of b*; $SD_{\Delta E}$, standard deviation of ΔE

the L* values decreased while the a* and b* values of coordinates increased over that of the virgin molded polymer and are in accordance with the results from biocomposites without modifier.

However, PCL- modified composites with 15% inclusion rate of fibres has shown highest values of L* compared with the composites without modifier. This could be attributed to the addition of 15% of modifier into the matrix as the sheet appeared to be lighter in color. Also, the color index values for each modified composite of PLA were higher than unmodified PLA composites.

4.3 Density

The unit density of molded biocomposites with biodegradable polymers and fibres is tabulated in Table 4.4 and comparison of means was done by Duncan's multiple range test. In both PLA and PCL biocomposites, the fibre loading of composites with all three types of fibres resulted in an increased density of the molded material. The results are in accordance with the literature review, as PP-flax fibre composites density has also been increased with addition of fibres (Soleimani et al. 2008). This could be because of the higher density of fibres than biodegradable polymers such as PLA and PCL. However, there was no significant effect of fibre treatment on the density of composites.

In PLA biocomposites, density of the formulated biocomposites varied from 1.272 to 1.302 g/cm^3 depending upon AHB, CRB-30, and CRB-65 fibre types, while the density of virgin PLA was found to be 1.250 g/cm^3. Similarly, in PCL biocomposites, the density of composites was higher as compared to virgin PCL, which was 1.144 g/cm^3. The densities of biocomposites filled with 15% of AHB, CRB-30, and CRB-65 fibres for PCL were 1.171, 1.180, and 1.185 g/cm^3, respectively.

Moreover, it has also been observed that with increase in fibre loading from 15% to 30%, the density of biocomposites increased for all formulations of PLA and PCL. For example, in case of PLA with AHB fibres, as fibres were added from 15% to 30%, the density increased from 1.272 to 1.297 g/cm^3, respectively. The same trend was observed in PCL biocomposites with CRB-65 fibre type, where density of composites with 30% fibre loading was higher upto 1.208 g/cm^3.

Table 4.4. Effect of formulations on the unit density of molded material with standard deviation (SD) and comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e,f for PLA and A,B,C,D,E for PCL formulation types.

Polymer	Fibre	Formulation (%)	Density of molded composites	
		Polymer/fibre	(g/cm^3)	SD
PLA	-	100/0	1.250^{f}	±0.0040
	AHB	85/15	1.272^{e}	±0.0015
		70/30	1.297^{b}	±0.0020
	CRB-30	85/15	1.272^{e}	±0.0071
		70/30	1.283^{c}	±0.0015
	CRB-65	85/15	1.276^{d}	±0.0021
		70/30	1.302^{a}	±0.0020
PCL	-	100/0	1.144^{E}	±0.0001
	AHB	85/15	1.171^{D}	±0.0010
		70/30	1.206^{A}	±0.0012
	CRB-30	85/15	1.180^{C}	±0.0015
		70/30	1.207^{A}	±0.0035
	CRB-65	85/15	1.185^{B}	±0.0011
		70/30	1.208^{A}	±0.0015

SD, standard deviation

On the other hand, the unit densities of biocomposites with addition of impact modifier are presented in the Table 4.5. In both PLA and PCL biocomposites, formulations containing 30% fibre loading have high density values in comparison to biocomposites with 15% fibre loading.

Apart from this, composites with 15% fibre loading had similar densities to that of virgin molded material; the reason could be because of lower density of impact modifier which was 0.940 g/cm^3 and lower fibre content with less percentage of polymer.

Table 4.5. Effect of formulations on the unit density of the molded material with standard deviation (SD) and comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b for PLA and A,B,C,D for PCL formulation type with chemical modifier (BS) and cellulose-rich fibres (CRB).

Polymer	Fibre	Formulation (%)	Density of molded composites	
		Polymer/BS/fibre	(g/cm^3)	SD
PLA	-	100/0/0	1.250^{a}	±0.0040
	CRB-30	70/15/15	1.214^{b}	±0.0016
		55/15/30	1.254^{a}	±0.0031
	CRB-65	70/15/15	1.236^{a,b}	±0.0309
		55/15/30	1.243^{a}	±0.0007
PCL	-	100/0/0	1.144^{C}	±0.0001
	CRB-30	70/15/15	1.141^{C,D}	±0.0010
		55/15/30	1.171^{B}	±0.0019
	CRB-65	70/15/15	1.139^{D}	±0.0004
		55/15/30	1.174^{A}	±0.0026

SD, standard deviation

4.4 Water absorption

The water absorption characteristics of PLA and PCL biocomposites are shown in Figures 4.1, 4.2, 4.3, and 4.4 (the error bar represents 1 standard deviation above and below the average). The literature review is effectively connected with the results of water absorption, which shows the hydrophilic nature of fibres are evident according to an increase in water absorption characteristics with fibre loading (Soleimani et al. 2008; Soleimani and Tabil 2012).

For molded PLA- and PCL-based biocomposites without modifier, approximately 0% to 2% increase in weight was observed and ANOVA of composites showed that weight increase was significantly dependent on fibre loading ($p = 0.05$). The lowest values of water uptake were associated with virgin polymers around 0.33% in PLA and 0.29% in PCL. However, it started rising with incorporation of fibre from 15% to 30% in each formulation from approximately 0.50% to 2.0% in biocomposites with no impact modifier. For PLA composites without impact modifier, with 15% to 30% fibre loading, acid-treated composites (AHB) showed the lowest absorption of water (approximately 0.58% to 0.93%) followed by CRB-30 composites (approximately 0.87% to 1.47%) and highest with CRB-65 composites (approximately 1.11% to 2.04%). On the other hand, water uptake in PCL composites followed the same trend as PLA but with almost same absorption in alkaline treated (CRB-30 and CRB-65) composites. These results are in accordance with the studies that report natural fibres have high affinity for water absorption (Soleimani et al. 2008; Li et al. 2009; Dehabadi and Wilson 2014).

Moreover, biocomposites with CRB fibres, with and without modifier were coupled in the graphs for PLA and PCL to see the effect of water absorption as shown in Figure 4.3 and 4.4. The water absorption capacity of composites increased as the fibre loading varied from 15% to 30%. Simultaneously, the water uptake for modified composites with 30% fibre loading almost doubled when compared to composites without chemical modification for both formulations containing PLA and PCL. The observed effect may be due to the hydrophilic nature of the material containing the higher percentage of fibre and weak adhesion to the polymer matrix.

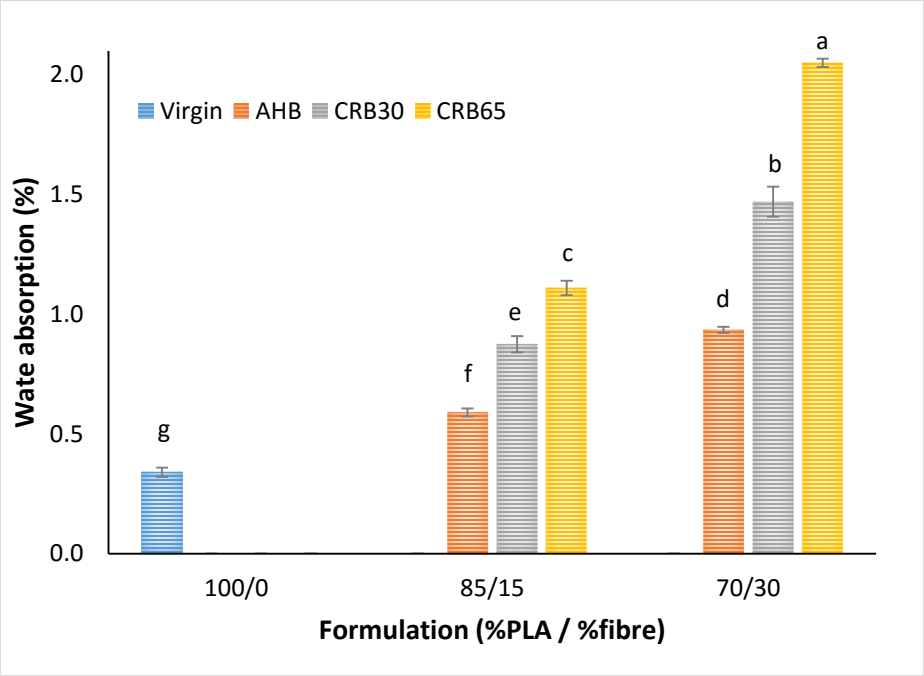


Figure 4.1. Water absorption (Eq. 3.5) of PLA-based biocomposites and comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e,f. Error bar represents 1 standard deviation above and below the average.

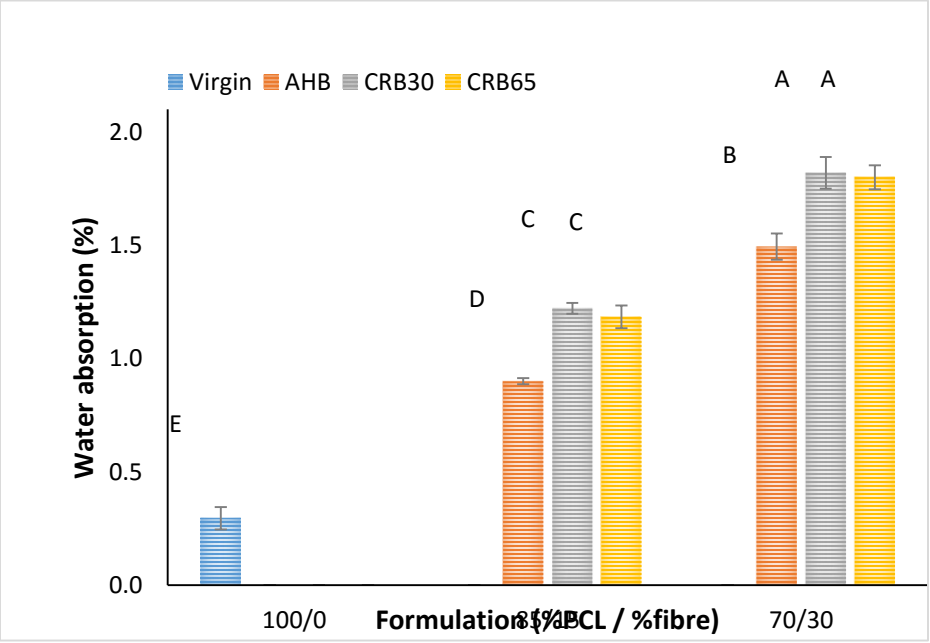


Figure 4.2. Water absorption (Eq. 3.5) of PCL-based biocomposites and comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E. Error bar represents 1 standard deviation above and below the average.

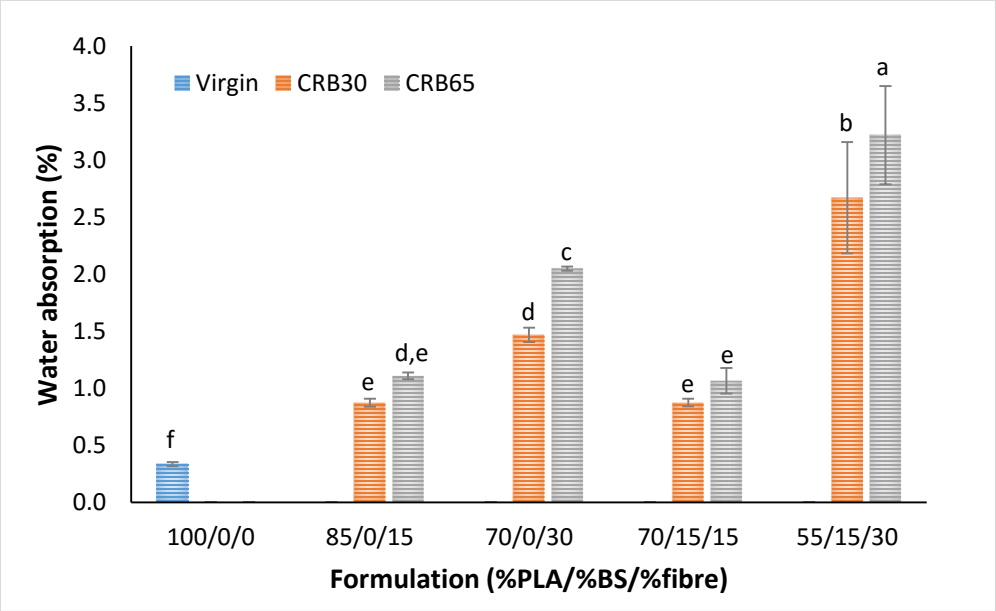


Figure 4.3. Water absorption (Eq. 3.5) in modified-alkaline PLA biocomposites and comparison with PLA biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e,f). Error bar represents 1 standard deviation above and below the average.

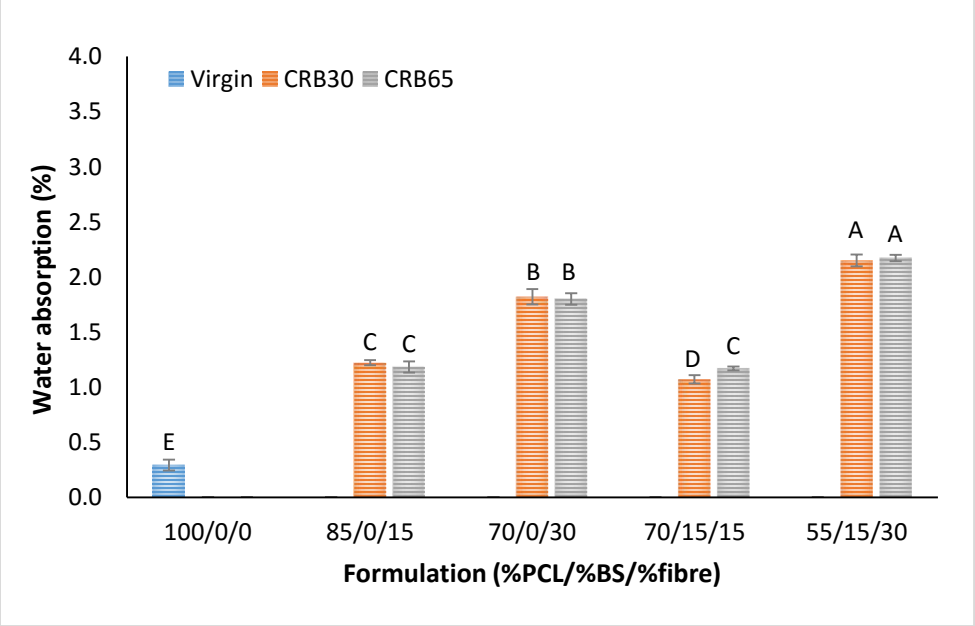


Figure 4.4. Water absorption (Eq. 3.5) in modified-alkaline PCL biocomposites and comparison with PCL biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated with A,B,C,D,E). Error bar represents 1 standard deviation above and below the average.

4.5 Tensile properties

The results for tensile strength and Young's modulus are presented in Figure 4.5-4.8 (where error bar represents 1 standard deviation above and below the average) for PLA- and PCL-based composites without impact modifier and statistically shown by ANOVA that verify that such properties are dependent on the different composite formulations ($p = 0.05$). These results are in favourable agreement with the study reported by Soleimani and co-workers (2008) for the effect of pre-treatment on the strength of PP-flax fibre composites. The tensile strength of the composites decreased with an increase in the fibre content in PLA and PCL formulations. For PLA, the strength of composites with 30% fibre loading decreased to almost half of the strength of virgin PLA. For example, the tensile strength of virgin PLA was approximately 46.2 MPa, but it decreased in composites loaded with 30% CRB-65 fibres where the tensile strength was only 18.7 MPa. On the other hand, CRB fibre formulations with 15% fibres showed higher strength than biocomposites with AHB fibres, as seen in the case of CRB-65 formulations with increased strength of 38.1 MPa. In PCL formulations, the tensile strength of biocomposites was slightly lower than virgin PCL which varied from 12.2 MPa to 15.6 MPa in composites with no impact modifier and was 16.0 MPa in virgin PCL. Moreover, the composites loaded with 15% fibres in both formulations had superior tensile strength than composites loaded with 30% fibres which could be due to poor stress-transfer from the polymer matrix to fibre (Soleimani et al. 2008).

In contrast to tensile strength, Young's modulus of PLA and PCL composites showed an opposite trend, where it increased with an increase in fibre loading, in accordance with those reported elsewhere (Soleimani et al. 2008). The tensile modulus of PCL composites with 15% and 30% formulations increased from 0.33 GPa (virgin) to 0.58 GPa and 0.90 GPa, respectively.

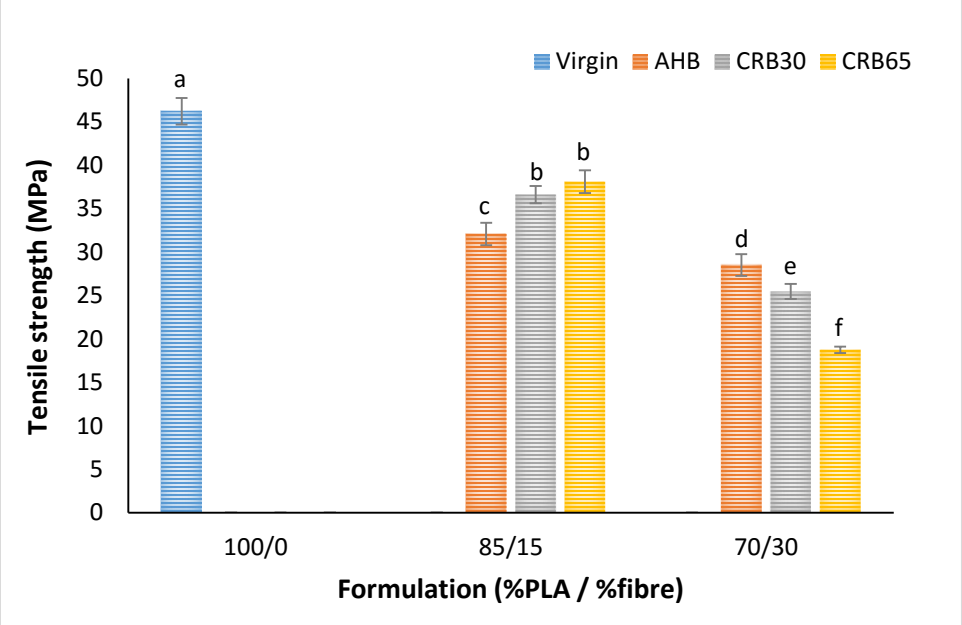


Figure 4.5. Tensile strength of PLA-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e,f for PLA formulation types. Error bar represents 1 standard deviation above and below the average.

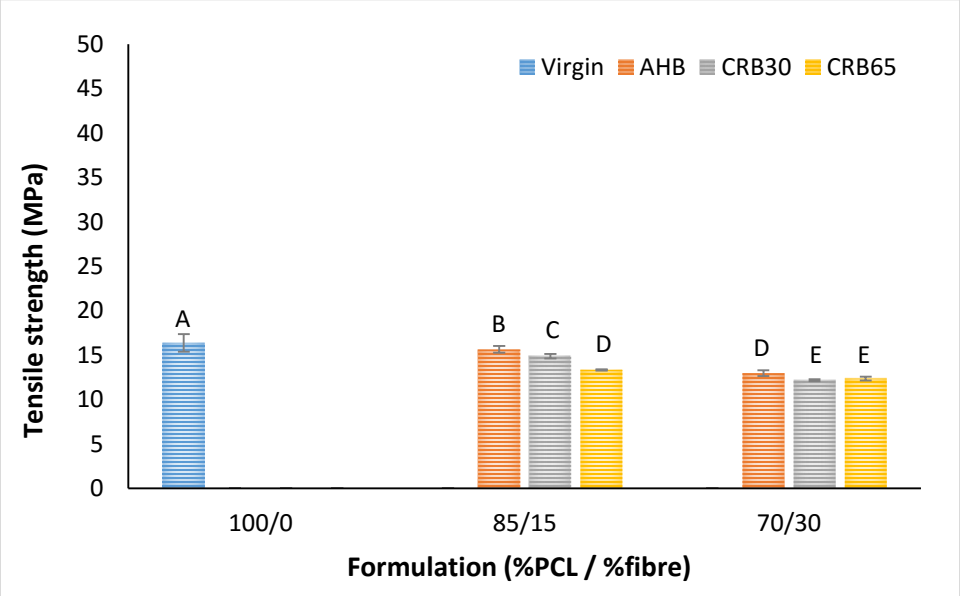


Figure 4.6. Tensile strength of PCL-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E for PCL formulation types. Error bar represents 1 standard deviation above and below the average.

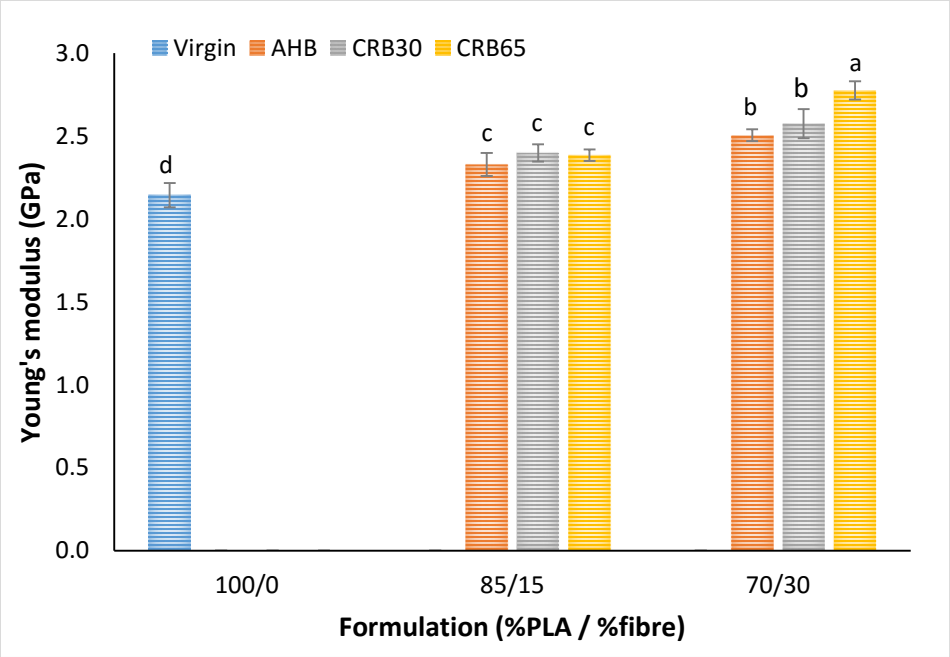


Figure 4.7. Tensile modulus (Young's modulus) of PLA-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as a,b,c,d for PLA formulation types. Error bar represents 1 standard deviation above and below the average.

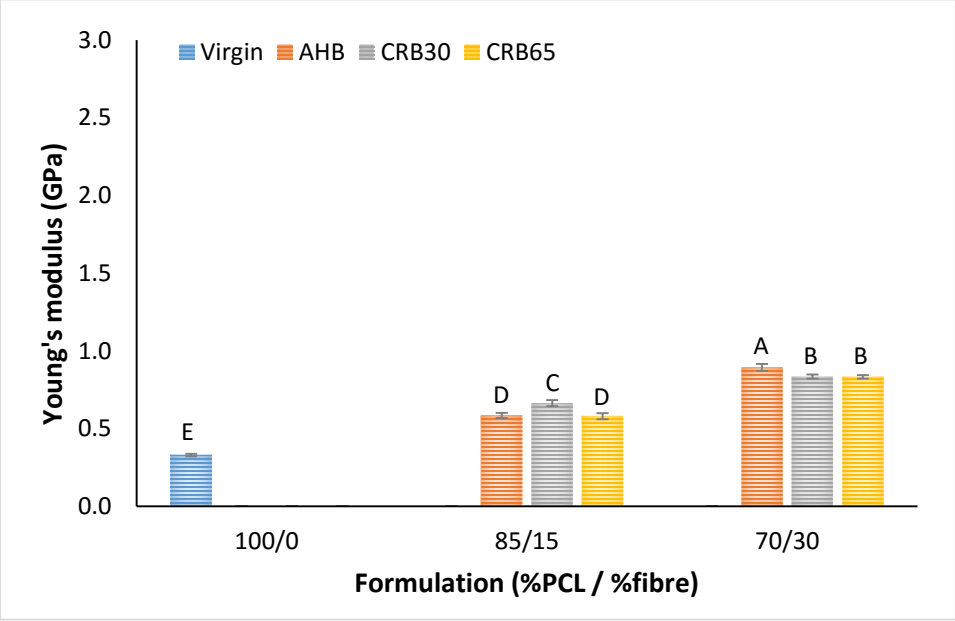


Figure 4.8. Tensile modulus (Young's modulus) of PCL-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E for PCL formulation types. Error bar represents 1 standard deviation above and below the average.

The mechanical properties of modified PLA- and PCL-based composites with alkaline-treated fibres are shown in Figure 4.9-4.12 (the error bar represents 1 standard deviation above and below the average). The tensile strength of biocomposites with impact modifier in both formulations of PLA and PCL decreased rapidly when compared against biocomposites without impact modifier, where the values are approximately halved. On the other hand, for PLA-based biocomposites with impact modifier, the Young's modulus was close to the virgin molded polymer for PLA. This was also similar result for alkaline-treated fibre PLA-based composites without impact modifier having values between 2.05 GPa to 2.20 GPa. The PCL-based biocomposites with impact modifier similarly had higher tensile modulus values than the virgin molded polymer, but the PCL-based biocomposites with no impact modifier still has the highest values of up to 0.84 GPa for alkaline-treated fibres.

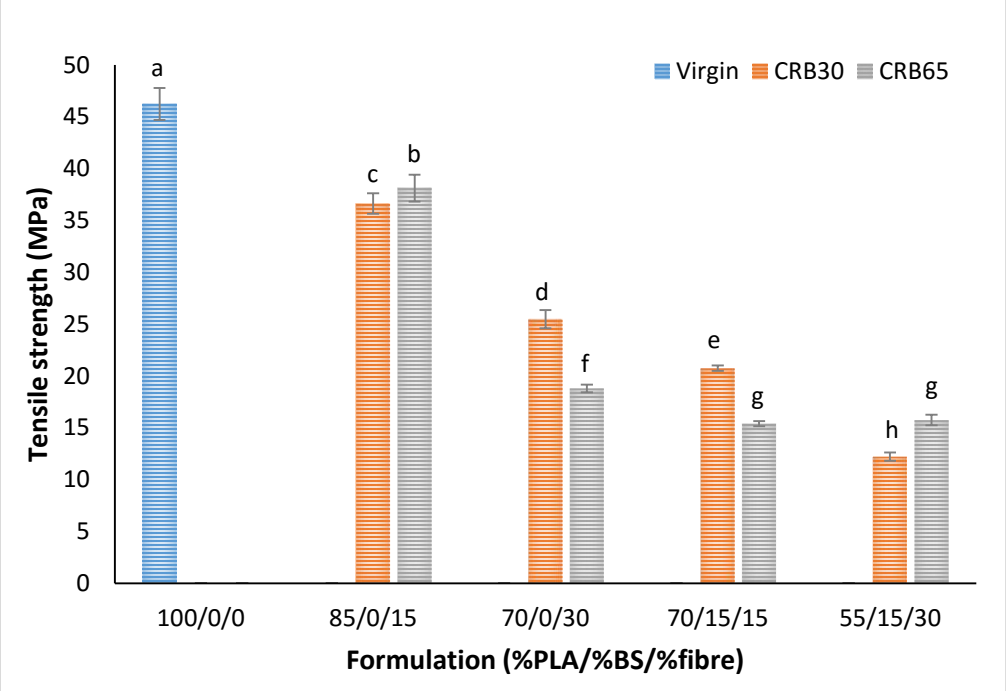


Figure 4.9. Tensile strength of modified-alkaline PLA biocomposites and comparison with PLA biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e,f,g,h). Error bar represents 1 standard deviation above and below the average.

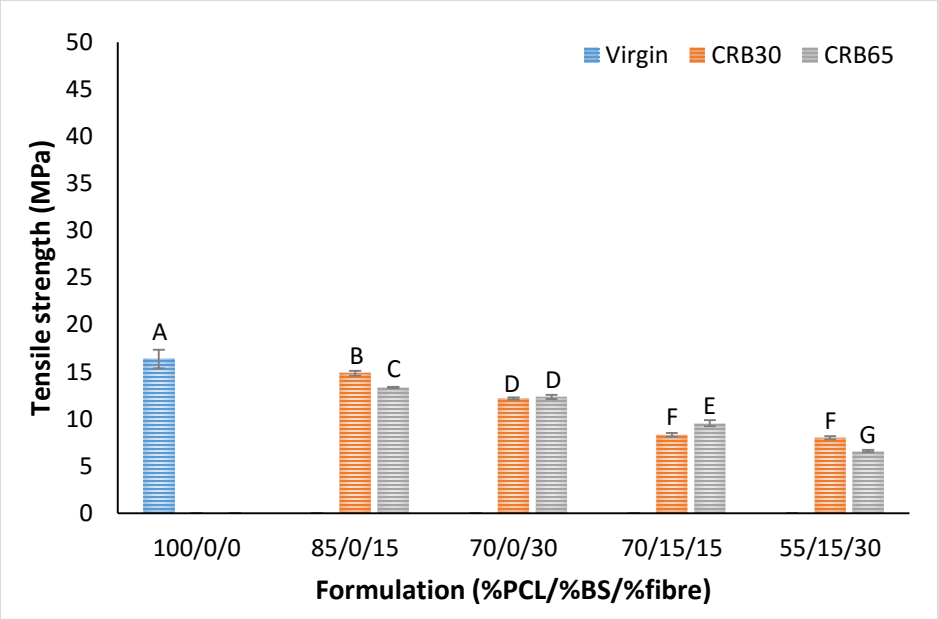


Figure 4.10. Tensile strength of modified-alkaline PCL biocomposites and comparison with PCL biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F,G). Error bar represents 1 standard deviation above and below the average.

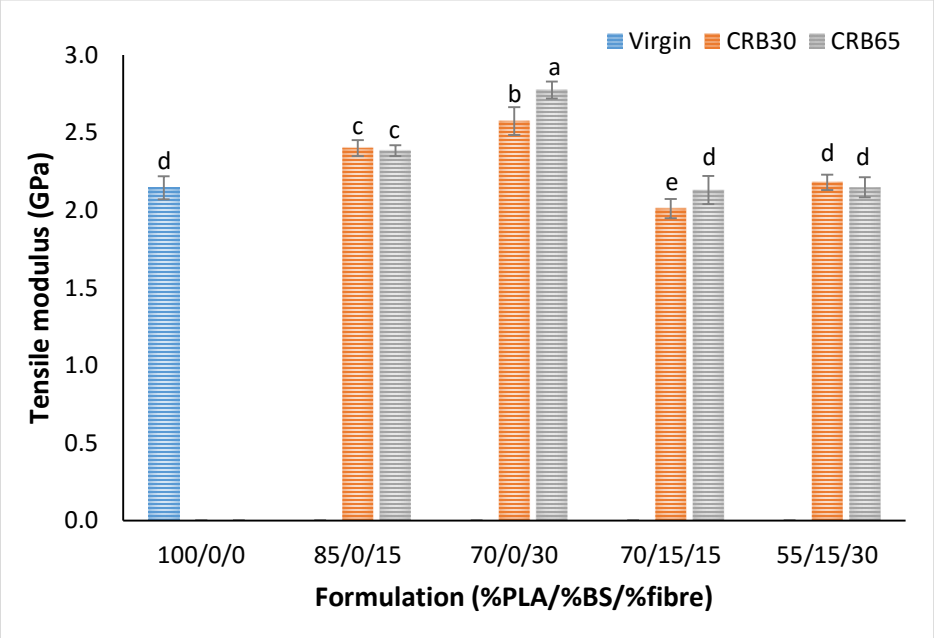


Figure 4.11. Tensile modulus of modified-alkaline PLA biocomposites and comparison with PLA biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e). Error bar represents 1 standard deviation above and below the average.

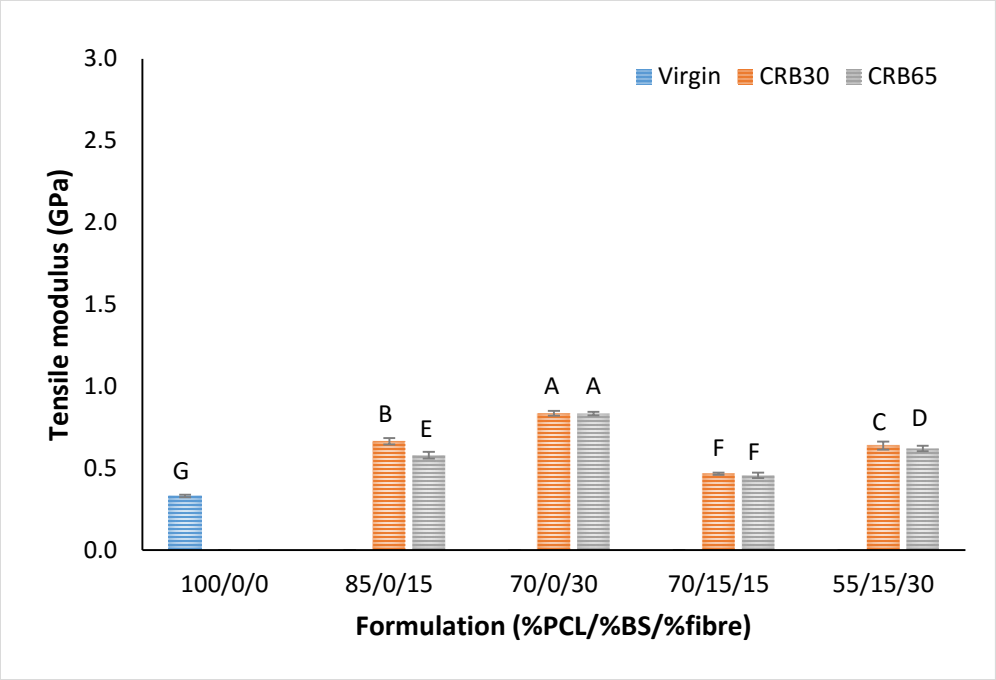


Figure 4.12. Tensile modulus of modified-alkaline PCL biocomposites and comparison with PCL biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F,G). Error bar represents 1 standard deviation above and below the average.

4.6 Flexural properties

Flexural properties for PLA- and PCL-based biocomposites without and with impact modifier are shown in Figure 4.13-4.20 (the error bar represents 1 standard deviation above and below the average), respectively. ANOVA of composites showed that flexural properties were affected with increase in fibre content (p = 0.05). For PLA, the flexural strength of virgin polymer was the highest and it started decreasing with increase in fibre content from 15% to 30%. While, in PCL composites, the bending strength of virgin PCL was 20 MPa and began to increase slightly with fibre content from 15 % to 30% with corresponding values of 23.71 MPa to 27.84 MPa, respectively. Using impact modifier on PLA-based biocomposites, a resulting sharp drop in the flexural strength was observed when compared to virgin PLA and PLA-based biocomposites

without impact modifier. Meanwhile, the bending strength of PCL-based biocomposites decreased as a result due to the use of modifier from 19.54 to 15.01 MPa.

The flexural modulus of PLA-based biocomposites without impact modifier increased slightly with fibre loading, however; the modulus of virgin polymer was almost the same in some cases. Moreover, flexural modulus for PCL composites almost doubled with the increase in fibre content with values from 0.45 GPa (for virgin PCL) to 1.33 GPa. The use of impact modifier in PLA-based composites resulted in a decrease of the flexural modulus with increasing fibre content. For PCL-based biocomposites containing an impact modifier, an increased flexural modulus was observed when compared to that of the virgin molded polymer. However, a much lower flexural modulus is observed compared with PCL-based biocomposites without impact modifier. This could be caused by structural characteristics of impact modifier, as if there was weak adhesion between the impact modifier and PCL matrix.

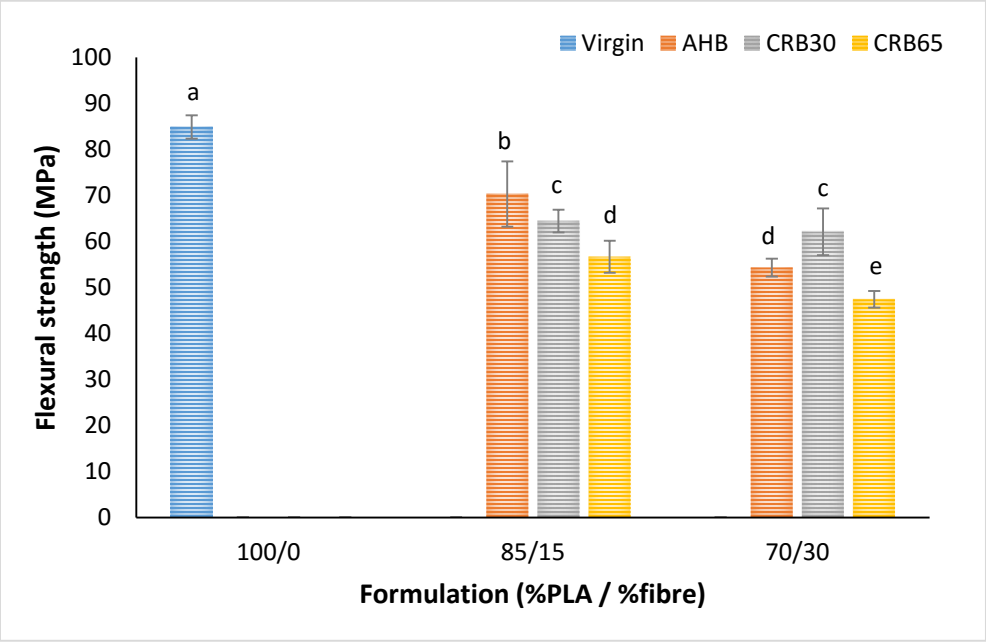


Figure 4.13. Flexural strength of PLA-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e for PLA formulation types. Error bar represents 1 standard deviation above and below the average.

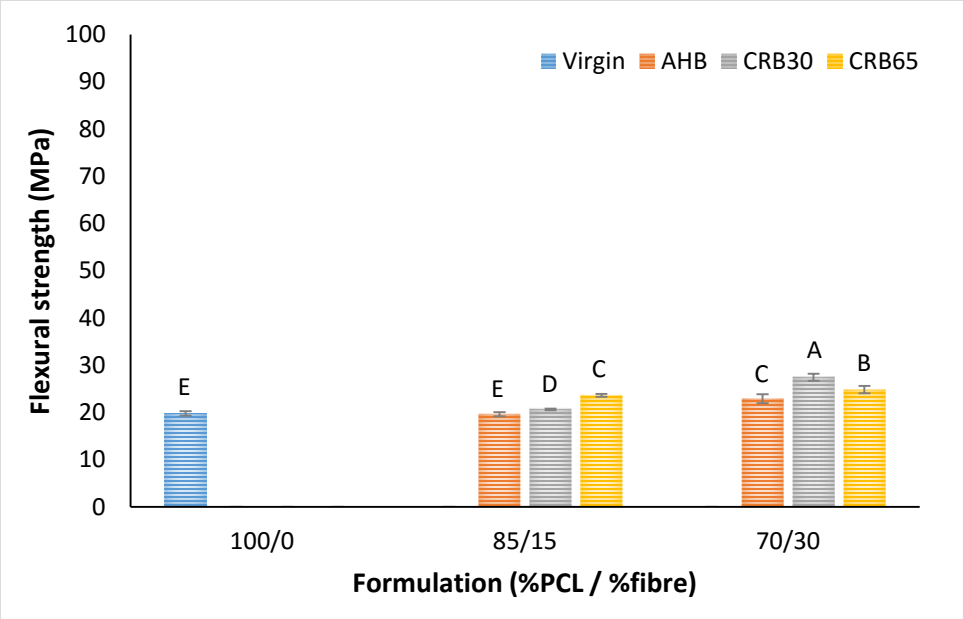


Figure 4.14. Flexural strength of PCL-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E for PCL formulation types. Error bar represents 1 standard deviation above and below the average.

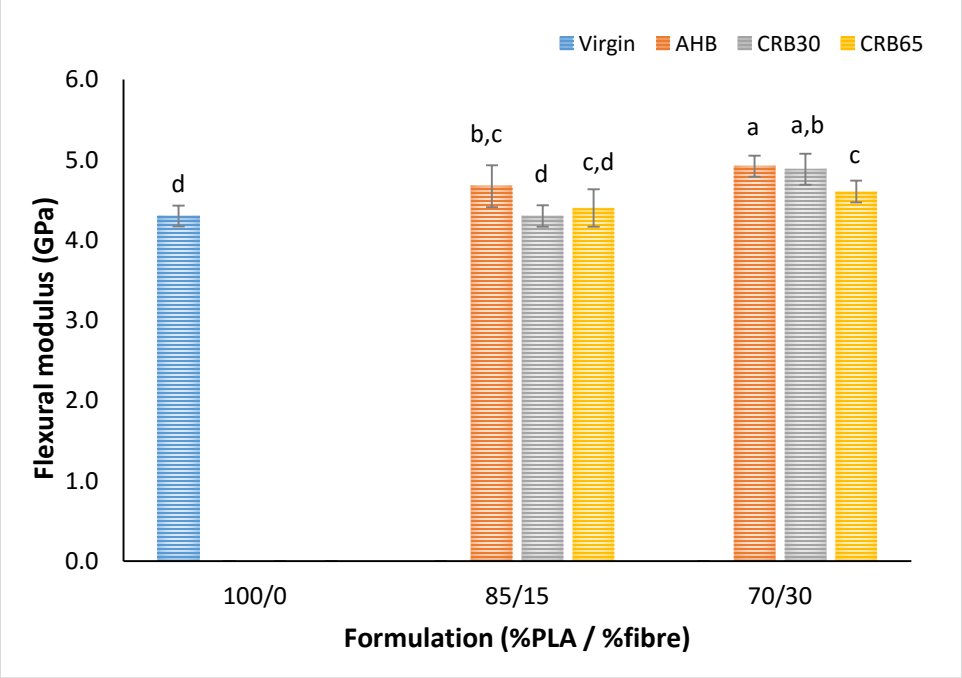


Figure 4.15. Flexural modulus of PLA-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as a,b,c,d for PLA formulation types. Error bar represents 1 standard deviation above and below the average.

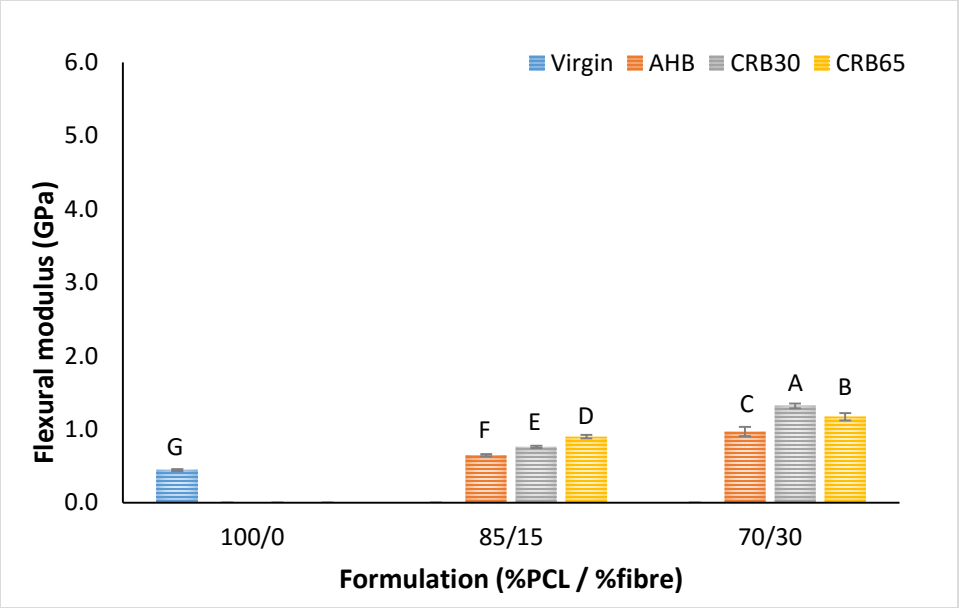


Figure 4.16. Flexural modulus of PCL-based biocomposites and comparison of means is shown by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F,G for PCL formulation types. Error bar represents 1 standard deviation above and below the average.

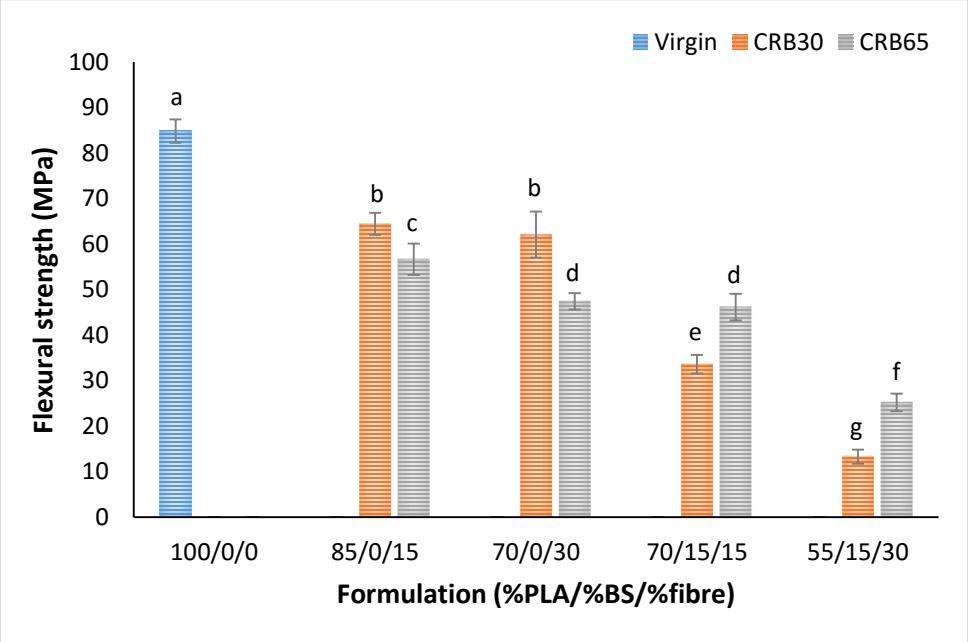


Figure 4.17. Flexural strength of modified-alkaline PLA biocomposites and comparison with PLA biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e,f,g). Error bar represents 1 standard deviation above and below the average.

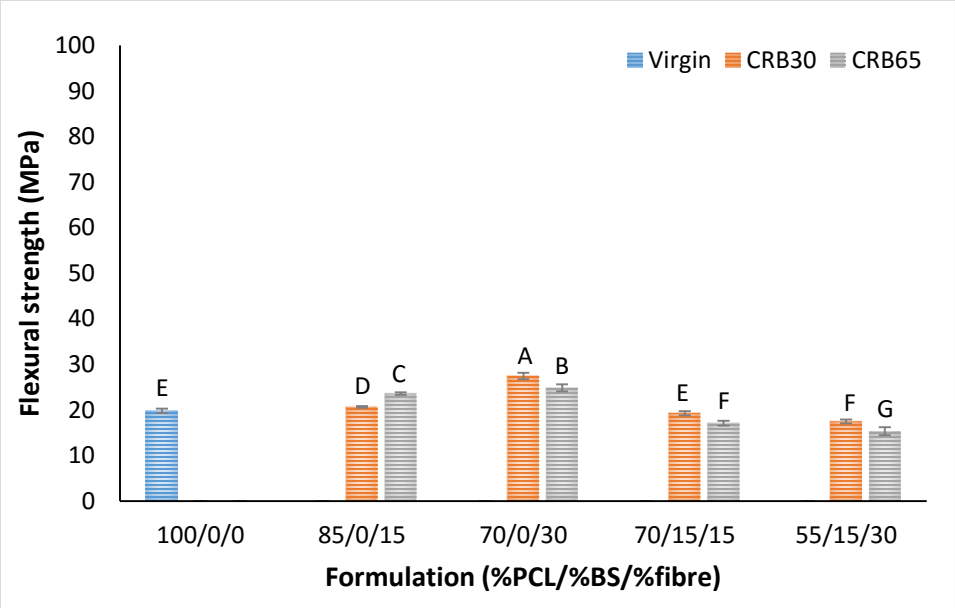


Figure 4.18. Flexural strength of modified-alkaline PCL biocomposites and comparison with PCL biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F,G). Error bar represents 1 standard deviation above and below the average.

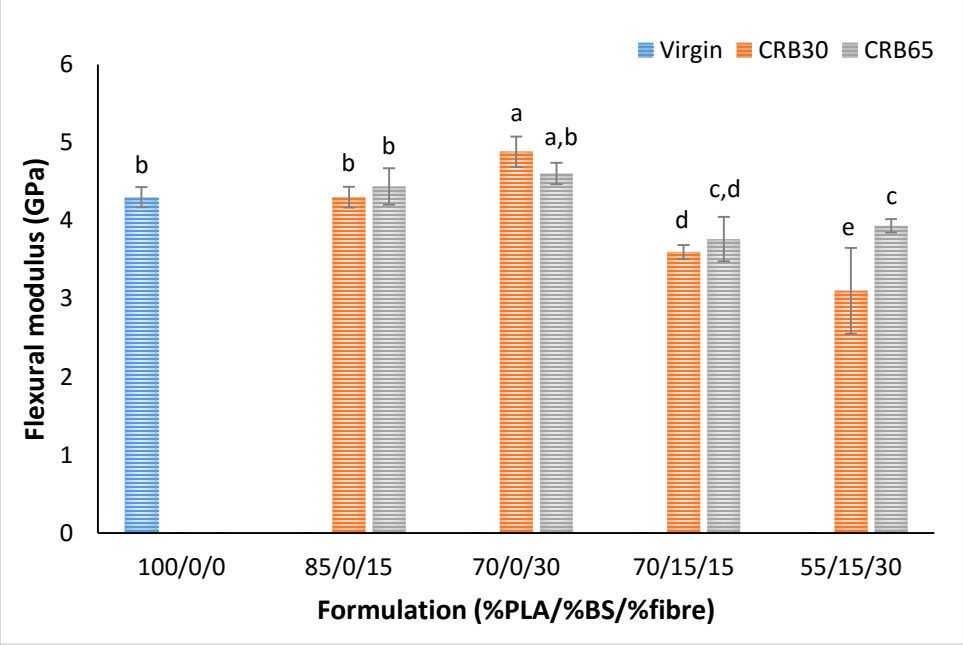


Figure 4.19. Flexural modulus of modified-alkaline PLA biocomposites and comparison with PLA biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e). Error bar represents 1 standard deviation above and below the average.

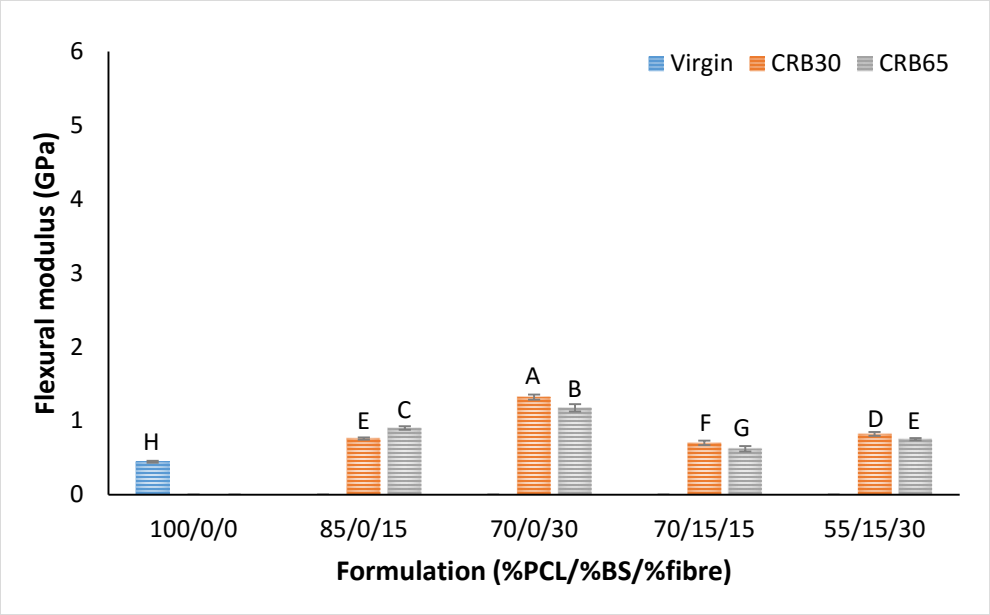


Figure 4.20. Flexural modulus of modified-alkaline PCL biocomposites and comparison with PCL biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F,G). Error bar represents 1 standard deviation above and below the average.

4.7 Tensile-impact properties

As discussed in the previous chapter, impact strength of the biocomposites was measured using tensile-impact testing machine. Results of tensile-impact test without impact modifier are shown in Figure 4.21 and 4.22 (where error bar represents 1 standard deviation above and below the average) for PLA and PCL composites, respectively. Statistical analysis with ANOVA revealed that fibre addition had a significant effect on the strength of composites. The impact strength of composites decreased with addition of fibres in both polymers. Biocomposites with AHB fibres have revealed higher impact strength than biocomposites with CRB fibres in all formulation types of PLA and PCL.

In PLA, the strength of composites with inclusion of 15% and 30% fibres is almost the same depending upon the types of fibre, but lower than virgin PLA. By comparison with PCL, the impact strength of biocomposites loaded with 15% fibres was higher than those with 30% fibre

loading. Moreover, in PCL containing composites, the impact strength was reduced gradually from AHB formulation to CRB-30, and then followed by CRB-65.

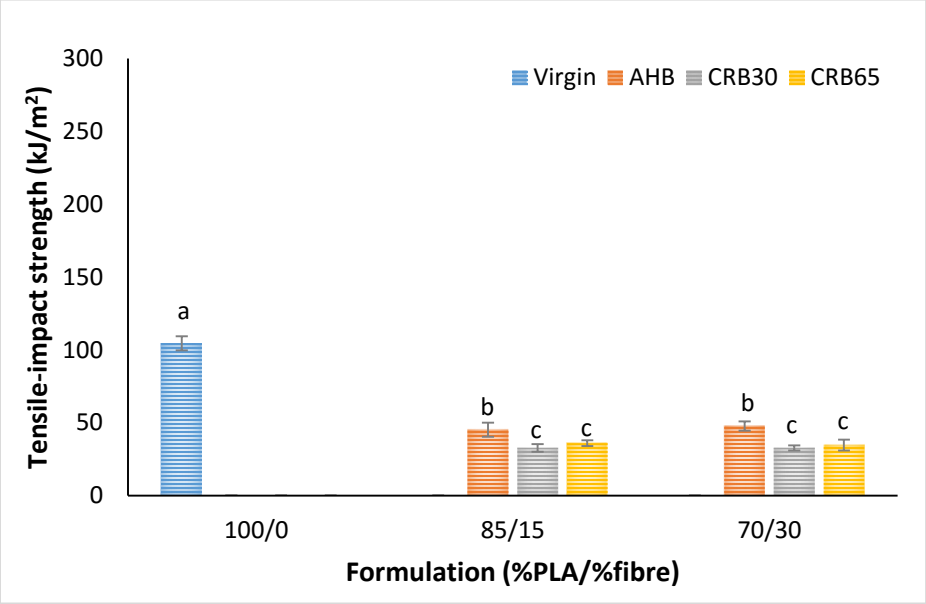


Figure 4.21. Tensile-impact strength of PLA-based biocomposites (unmodified) and comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c. Error bar represents 1 standard deviation above and below the average.

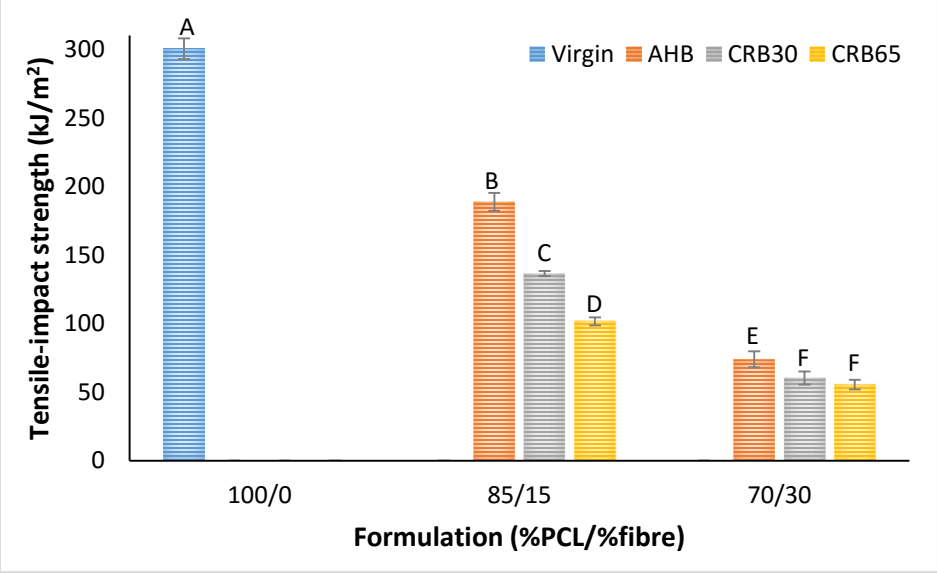


Figure 4.22. Tensile-impact strength of PCL-based biocomposites (unmodified) and comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F. Error bar represents 1 standard deviation above and below the average.

The influence of impact modifier in PLA and PCL biocomposites are shown in Figure 4.23 and 4.24 (the error bar represents 1 standard deviation above and below the average). The addition of Biomax Strong (impact modifier) is supposed to increase the impact properties of PLA. In all formulations of PLA and PCL, 15% of impact modifier is added to the polymer matrix and fibres. The combination of impact modifier with alkaline-treated fibres revealed promising results as evidenced by the tensile-impact strength of biocomposites according to the increase relative to biocomposites without impact modifier.

In PLA, composites with 15% of CRB-30 fibres and impact modifier exhibited the highest tensile-impact strength of 187.70 kJ/m^2; while the virgin molded polymer had an impact strength of 104.52 kJ/m^2. On the other hand, the strength of biocomposites without impact modifier loaded with 15% CRB-30 fibres was only 32.65 kJ/m^2. Similarly, PCL-based biocomposites with impact modifier had higher impact strength values than PCL-based biocomposites without impact modifier with 15% and 30% inclusion of fibres. However, molded virgin PCL had greater impact strength than modified composites with a value of 300.306 kJ/m^2; this could be due to the higher flexibility of virgin PCL in comparison to matrix with fibres (Liu and Zhang 2011; Pilla 2011; Jimenez et al. 2014).

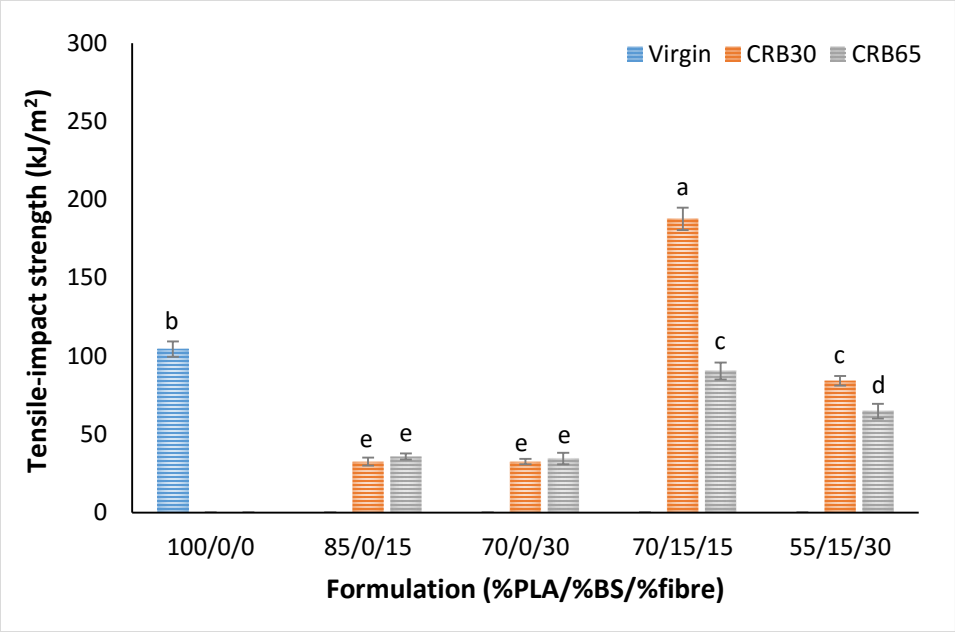


Figure 4.23. Tensile-impact strength of modified-alkaline PLA biocomposites and comparison with PLA biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as a,b,c,d,e). Error bar represents 1 standard deviation above and below the average.

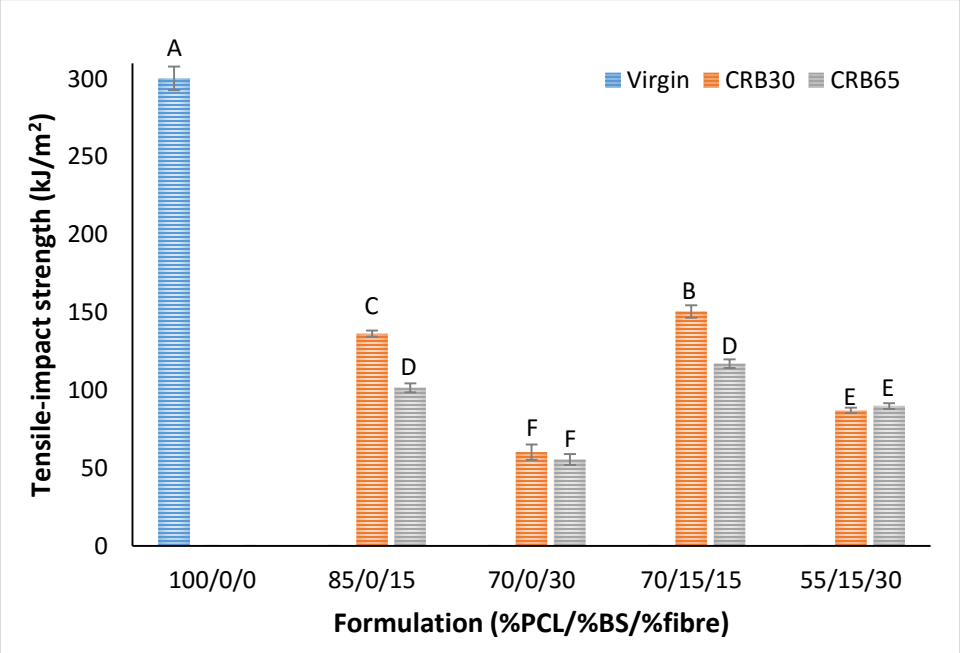


Figure 4.24. Tensile-impact strength of modified-alkaline PCL biocomposites and comparison with PCL biocomposites without impact modifier (comparison of means by Duncan's multiple range test (p = 0.05) designated as A,B,C,D,E,F). Error bar represents 1 standard deviation above and below the average.

5. SUMMARY AND CONCLUSIONS

In this research project, biocomposites were developed from oat hulls and biodegradable polymers using extrusion and compression molding techniques. The mechanical and physical properties related to the biocomposites were also examined.

5.1 Summary

Oat hull, an abundant biomass in Canada is a by-product of oat processing. It has high fibre content which may be used as a reinforcement or filler for the production of biocomposites in combination with PLA and PCL. The addition of fibres can also reduce the price of composites because of the very low cost of this biomass by-product. Moreover, biocomposites made with natural fibres and biodegradable polymers are shown to be environmental friendly products which could reduce the use of petroleum-based materials.

In this study, oat hulls were subjected to dilute acid hydrolysis and alkaline treatment to produce three different types of fibres, namely, AHB, CRB-30, and CRB-65. The fibres were successfully incorporated into the polymer matrix with PLA and PCL in different formulations. The impact modifier, Biomax Strong 120, was used in order to improve the impact strength and toughness of PLA. The formulations were extruded through twin-screw extruder for better dispersion of fibre into the polymer matrix and then compression molded. The physical and mechanical properties of manufactured biocomposites such as color, density, water absorption, tensile strength, tensile modulus, flexural strength, flexural modulus, and tensile-impact strength were studied.

Chemical analysis confirmed the reduction of hemi-cellulose and lignin in the fibres with corresponding increase in cellulose content. Dilute-acid hydrolysis eliminated the hemi-cellulose fraction which resulted in isolation of the cellulose and lignin fractions.

The color analysis of nearly all of the biocomposite formulations (un-modified and modified) revealed the lowest L* values with highest a* and b* values, indicating that fibre addition resulted in darkening of the biocomposites; otherwise, no significant effect of fibre loading was observed.

The water absorption values of composites revealed that the hydrophilic behavior of natural fibres; composites based on AHB fibres showed lower water uptake than composites based on CRB fibres which means that the modification of fibres with alkaline treatment was not affected according to the water absorption characteristics. While modified alkaline-treated composites with Biomax Strong 120, had the highest water absorption among all formulations (with 30% fibre loading). The mechanical properties of PLA composites (especially tensile modulus and flexural modulus) were higher than virgin polymer. On the other hand, PCL composites showed more effective results towards all tensile and flexural properties with fibres as reinforcement. The impact modifier used in this study had a positive effect on the tensile-impact properties of PLA and PCL biocomposites containing oat hull fibres.

Moreover, biocomposites were successfully developed containing PLA and PCL, where favourable results similar to flax fibre-PP composites as reported by Soleimani and co-workers (2008). In addition, this research has demonstrated several different ways to utilize high volume oat hull biomass by manufacturing environmentally friendly bioproducts. Simultaneously, significant contribution of biodegradable polymers and fibres in this study has addressed superior mechanical properties of biocomposites as well as their improved biodegradability in comparison

to composites made from polyethylene or polypropylene (Soleimani et al. 2008; Li et al. 2009; Soleimani and Tabil 2012).

5.2 Conclusions

The specific objectives of this study were to investigate the inclusion rate of three different types of fibres with PLA and PCL, and to study their physical and mechanical properties. The following conclusions are made based on the experimental results and analysis of the data:

5.2.1 Effect of fibre loading of AHB on PLA and PCL biocomposites

1. For PLA-based biocomposite, an increase in the fibre loading (15% to 30%) showed an increased density, water absorption, Young's modulus and flexural modulus of biocomposites. By contrast, the tensile strength, flexural strength and tensile-impact strength decreased when compared with virgin molded PLA. In contrast to composites with alkaline-treated fibres, the tensile and impact properties revealed promising results in composites with acid-treated fibres.
2. For PCL biocomposites, properties like density, water absorption, Young's modulus, flexural strength and flexural modulus were enhanced with an increase in fibre loading. On the other hand, tensile strength and impact strength of composites were reduced with addition of fibres; but displayed superior properties with composites containing alkaline-treated fibres.

5.2.2 Effect of inclusion rate of delignified fibres (CRB-30 and CRB-65) on PLA and PCL biocomposites

1. In PLA-based biocomposites, physical properties such as unit density and water absorption increased with an increase in fibre loading (15% to 30%) with higher values observed in CRB-65 fibres; whereas, composites with alkaline-treated fibres exhibited lower tensile, flexural, and impact strength than virgin PLA.

2. The mechanical properties associated with alkaline-treated fibres in PCL-based biocomposites showed excellent results, except in tensile-impact strength. The density of composites was greater than virgin and acid-treated fibre composites. However, alkaline-treated composites were not significantly affected by fibre loading. Further, water absorption characteristics of alkaline-treated composites increased with fibre addition from 15% to 30%.

5.2.3 Effect of impact modifier on modified PLA and PCL biocomposites

Biomax Strong 120, was used to improve the impact properties of biocomposites. It was more effective and efficient for improving the impact strength of PLA and PCL biocomposites.

In modified-PLA biocomposites, there was no significant change in the density of biocomposites over that of virgin PLA which remained approximately the same. On the contrary, modified-PCL biocomposites with 30% fibre loading exhibited higher density than virgin PCL. On the other hand, water absorption properties of PLA and PCL composites were significantly affected by inclusion of fibres.

The tensile-impact properties of modified composites with PLA and PCL displayed increased impact strength with impact modifier addition; while other mechanical properties like tensile and flexural strength were negated.

6. RECOMMENDATIONS

For future research work, the following recommendations are made:

1. In this study, biocomposites were developed by compression molding technique. Other molding techniques such as injection molding may be considered to manufacture composites.
2. PLA can be blended with other biodegradable and biocompatible polymers such as PCL to broaden its applications. Polyglycolic acid (PGA), a bio-based polymer may be examined to develop bioproducts since it is stronger than PLA.
3. Biocomposites exhibited higher water absorption characteristics due to hydrophilic nature of fibres. In order to overcome this problem, different surface modifications of fibres should be considered.
4. Some additional properties such as thermal, rheological, and morphological should be studied for future research work of molded biocomposites and biofibres.
5. There is a need to study biodegradation of composites for the durability of the product and sustainable environment.
6. Optimizing the effect of different particle size of fibres in molding techniques may be investigated in future work.
7. Optimization of processing conditions in extrusion and compression molding techniques with different surface treatments for better properties of fibre-reinforced products.

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APPENDIX

APPENDIX

Table A1. Water absorption of PLA- and PCL-based biocomposites.

Polymer	Fibre	Formulation(%)	Water absorption	
		Polymer/fibre	(%)	SD
PLA	-	100/0	0.337	±0.019
	AHB	85/15	0.590	±0.017
		70/30	0.935	±0.013
	CRB-30	85/15	0.875	±0.034
		70/30	1.470	±0.063
	CRB-65	85/15	1.110	±0.030
		70/30	2.05	±0.017
PCL	-	100/0	0.295	±0.050
	AHB	85/15	0.900	±0.013
		70/30	1.494	±0.058
	CRB-30	85/15	1.222	±0.024
		70/30	1.820	±0.070
	CRB-65	85/15	1.184	±0.050
		70/30	1.800	±0.053

SD, standard deviation

Table A2. Water absorption of modified-alkaline PLA and PCL biocomposites.

Polymer	Fibre	Formulation (%)	Water absorption	
		Polymer/BS/fibre	(%)	SD
PLA	-	100/0/0	0.337	±0.019
	CRB-30	70/15/15	0.876	±0.033
		55/15/30	2.670	±0.488
	CRB-65	70/15/15	1.068	±0.112
		55/15/30	3.22	±0.431
PCL	-	100/0/0	0.295	±0.050
	CRB-30	70/15/15	1.072	±0.038
		55/15/30	2.150	±0.053
	CRB-65	70/15/15	1.170	±0.018
		55/15/30	2.171	±0.029

SD, standard deviation

Table A3. Tensile properties of PLA- and PCL-based biocomposites.

Polymer	Fibre	Formulation(%)	Tensile Strength		Tensile Modulus	
		Polymer/fibre	(MPa)	SD	(GPa)	SD
PLA	-	100/0	46.216	±1.544	2.144	±0.074
	AHB	85/15	32.103	±1.295	2.330	±0.070
		70/30	28.525	±1.246	2.505	±0.036
	CRB-30	85/15	36.627	±0.993	2.400	±0.052
		70/30	25.474	±0.880	2.575	±0.088
	CRB-65	85/15	38.105	±1.305	2.385	±0.035
		70/30	18.768	±0.370	2.775	±0.055
PCL	-	100/0	16.371	±0.994	0.330	±0.008
	AHB	85/15	15.653	±0.373	0.585	±0.016
		70/30	12.967	±0.330	0.894	±0.023
	CRB-30	85/15	14.868	±0.245	0.664	±0.019
		70/30	12.176	±0.111	0.835	±0.014
	CRB-65	85/15	13.345	±0.100	0.580	±0.020
		70/30	12.360	±0.220	0.833	±0.011

SD, standard deviation

Table A4. Tensile properties of modified-alkaline PLA and PCL biocomposites.

Polymer	Fibre	Formulation(%)	Tensile Strength		Tensile Modulus	
		Polymer/BS/fibre	(MPa)	SD	(GPa)	SD
PLA	-	100/0/0	46.216	±1.544	2.144	±0.074
	CRB-30	70/15/15	20.731	±0.264	2.010	±0.062
		55/15/30	12.212	±0.413	2.179	±0.049
	CRB-65	70/15/15	15.378	±0.252	2.130	±0.090
		55/15/30	15.745	±0.524	2.148	±0.065
PCL	-	100/0/0	16.371	±0.994	0.330	±0.008
	CRB-30	70/15/15	8.330	±0.210	0.466	±0.007
		55/15/30	8.020	±0.164	0.638	±0.024
	CRB-65	70/15/15	9.565	±0.337	0.456	±0.016
		55/15/30	6.572	±0.121	0.620	±0.016

SD, standard deviation

Table A5. Flexural properties of PLA- and PCL-based biocomposites.

Polymer	Fibre	Formulation(%)	Flexural Strength		Flexural Modulus	
		Polymer/fibre	(MPa)	SD	(GPa)	SD
PLA	-	100/0	84.864	±2.546	4.302	±0.126
	AHB	85/15	70.304	±7.080	4.672	±0.261
		70/30	54.300	±1.950	4.923	±0.132
	CRB-30	85/15	64.460	±2.458	4.300	±0.133
		70/30	62.113	±5.052	4.884	±0.195
	CRB-65	85/15	56.692	±3.472	4.440	±0.234
		70/30	47.441	±1.811	4.605	±0.136
PCL	-	100/0	19.784	±0.498	0.446	±0.013
	AHB	85/15	19.624	±0.444	0.648	±0.015
		70/30	22.880	±0.948	0.968	±0.063
	CRB-30	85/15	20.647	±0.170	0.758	±0.015
		70/30	27.454	±0.716	1.320	±0.033
	CRB-65	85/15	23.578	±0.310	0.900	±0.024
		70/30	24.835	±0.790	1.173	±0.050

SD, standard deviation

Table A6. Flexural properties of modified-alkaline PLA and PCL biocomposites.

Polymer	Fibre	Formulation(%)	Flexural Strength		Flexural Modulus	
		Polymer/BS/fibre	(MPa)	SD	(GPa)	SD
PLA	-	100/0/0	86.864	±2.546	4.302	±0.126
	CRB-30	70/15/15	33.623	±2.074	3.596	±0.090
		55/15/30	13.282	±1.517	3.102	±0.551
	CRB-65	70/15/15	46.184	±2.891	3.764	±0.286
		55/15/30	25.233	±1.950	3.935	±0.085
PCL	-	100/0/0	19.784	±0.499	0.446	±0.013
	CRB-30	70/15/15	19.270	±0.460	0.695	±0.029
		55/15/30	17.445	±0.433	0.820	±0.026
	CRB-65	70/15/15	17.084	±0.526	0.619	±0.036
		55/15/30	15.319	±0.899	0.749	±0.014

SD, standard deviation

Table A7. Tensile-impact properties of PLA- and PCL-based biocomposites.

Polymer	Fibre	Formulation(%)	Tensile-impact strength	
		Polymer/fibre	(kJ/m^2)	SD
PLA	-	100/0	104.520	±4.906
	AHB	85/15	45.151	±4.789
		70/30	47.724	±3.166
	CRB-30	85/15	32.652	±2.614
		70/30	32.653	±1.704
	CRB-65	85/15	35.934	±1.998
		70/30	34.625	±3.695
PCL	-	100/0	300.306	±7.602
	AHB	85/15	188.634	±6.583
		70/30	73.904	±5.747
	CRB-30	85/15	136.400	±1.903
		70/30	60.261	±4.880
	CRB-65	85/15	101.576	±2.927
		70/30	55.492	±3.465

SD, standard deviation

Table A8. Tensile-impact properties of modified-alkaline PLA and PCL biocomposites.

Polymer	Fibre	Formulation (%)	Tensile-impact strength	
		Polymer/BS/fibre	(kJ/m^2)	SD
PLA	-	100/0/0	104.520	±4.906
	CRB-30	70/15/15	187.700	±7.180
		55/15/30	84.230	±3.050
	CRB-65	70/15/15	90.490	±5.451
		55/15/30	64.830	±4.650
PCL	-	100/0/0	300.306	±7.602
	CRB-30	70/15/15	150.691	±4.020
		55/15/30	87.100	±1.800
	CRB-65	70/15/15	117.074	±2.780
		55/15/30	89.900	±1.846

SD, standard deviation